STUDIES ON THE NUTRIENT CHEMISTRY OF A TROPICAL ESTUARY

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IN
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TO MY PARENTS

CERTIFICATE

This is to certify that the Thesis bound herewith is an authentic record of the research carried out by Sri.T.S.Anirudhan, M.Phil., under my supervision and guidance in the Chemical Oceanography Division, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and no part thereof has been presented before for any other degree in any University.

Dr.P.N.K. NAMBISAN
(Supervising Teacher)

Cochin - 16
September, 1988

DECLARATION

I hereby declare that the thesis entitled "Studies on the Nutrient Chemistry of a Tropical Estuary" is an authentic record of research carried out by me under the supervision and guidance of Dr.P.N.K. Nambisan, Professor and Head, Chemical Oceanography Division, School of Marine Sciences, Cochin University of Science and Technology in partial fulfilment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and that no part of it has previously formed the basis for the award of any degree, diploma or associateship in any University.

T.S.ANIRUDHAN

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T.S. ANIRUDHAN

CONTENTS

PREFACE

Greater Cochin of area 731 km^2 is one of the most densely populated ($\simeq$ 1.5 million) urban conglomerates of South India, blessed with a network of waterways. In these days of increasing urbanization, industrialization and overall development, there is no doubt, that the problem of water pollution will be of great concern.

Like many other major estuarine systems, the Cochin estuary is also subjected to increasing human interferences; the waterway receives considerable amount of pollutants from (i) industrial units like Fertilizers and Chemicals Travancore Ltd., Travancore Cochin Chemicals, Indian Rare Earths, Hindustan Insecticides Ltd., Cochin Refineries etc. (ii) domestic sewage works and storm water channels (iii) port area handling large quantities of crude and refined petroleum products and industrial chemicals (iv) coconut husk retting yards and (v) fishery industries. The net effect of these discharges have caused irreparable damage to the flora and fauna of the water body; the productivity of this region has been considerably affected. It is, therefore, desirable to maintain and manage the estuarine ecosystem by way of upkeeping the water quality standards.

The knowledge on the various aspects of the physico-chemical parameters of this estuary turns out to be essential for assessing the water quality and various biogeochemical processes and also in providing future guidelines on the estuarine management/modifications. In this connection, the University Grants Commission (India) was pleased to approve a research project entitled "A comprehensive study of the Vembanad lake and adjacent coastal waters" operational at the School of Marine Sciences, Cochin University of Science and Technology, Cochin-16. The studies on the very many chemical aspects of Cochin estuary (part of Vembanad Kayal) were carried out in the Chemical Oceanography Division of the School and the work reported in this thesis forms part of the above project. The thesis is an attempt to study the nutrient chemistry of this tropical estuary.

ABBREVIATIONS

°C : degree celsius

cm : centimeter (s)

DO : dissolved oxygen

hr : hour(s)

IRP : inorganic reactive phosphorus

RSi : inorganic reactive silicate - silicon

l : litre

m : meter (s)

μ : micron

μg : micro gram = 10^{-6} g

μg at l^{-1} : μg atoms l^{-1}

PRP : particulate reactive phosphorus

10^{-3} : Parts per mille - Salinity (‰)

stn. : station (s)

TRP : total reactive phosphorus

CHAPTER 1

INTRODUCTION

The fast advancing technological development and population growth have had significant detrimental effects on the natural environment. Anthropogenic waste inputs of industrial, municipal and agricultural nature containing enormous quantities of toxic substances - both dissolved and suspended - into the water bodies cause serious water pollution problems. These substances have deleterious effects on the flora and fauna; the photosynthesis may be adversely affected, thus the primary production and hence higher trophic levels may be affected. The pollutant may be lethal to one or more of the various estuarine communities. Toxic elements may accumulate in the plant and animal tissues and by successive integration through the food web may finally reach man. In effectively combating such serious water pollution problems we require to know the chemical species and their concentrations present in the effluents and in the receiving waters, and their interactions.

Estuaries are recognised as areas of commercial, industrial and recreational activities and play an important role in the natural life cycle of some aquatic organisms. While development of coastal water bodies has contributed to significant economic advancement and social changes, it has also brought in severe environmental problems.

Though a few estuaries have been able to assimilate the waste loads depending on factors like mixing, flushing time and nature of the waste, many of the more remote and unspoilt estuaries of the world are in danger due to man's ruthless exploitation.

It is obvious that continuous discharge of industrial effluents tends to increase the pollutant loads in the aquatic environment; presence of excessive amounts of nutrients in effluents have led to cause eutrophication in receiving waters. Recently more attention has been given to solve problems of nutrient loading and also to control eutrophication. In this connection, studies on nutrient transport in some of the major rivers of the world ranging from Mississippi (USA), Nile (Egypt), Solimoes (Brazil) to Iton (France) have been reported by Meybeck (1982); the study also reported the source of nutrients and status of eutrophication in these rivers.

In recent years, there has been a rapidly growing interest in research on estuaries and their nutrient content, to probe into the nature and cause of pollution, and the pathways and means to control it. Chemical studies on lake Maryut, a polluted lake south of Alexandria, Egypt had helped to assess the degree of water pollution and probable causes of the decrease in fish production (Wahby _et al._, 1978). Quantitative study of nutrient fractionation and stoichiometric model of the Baltic Sea have been reported by Sen Gupta & Koroleff (1973); more recent work in Baltic is reported by Pastuszak (1985). The studies on chemical characteristics of estuaries like Hudson, USA (Simpson _et al._, 1975), Tamar, UK (Morris _et al._, 1981), Mandovi-Zuari, India (Qasim & Sen Gupta, 1981) and Delaware, USA (Sharp _et al._, 1982) have been useful in assessing the water quality of these bodies. The major chemical characteristics of seven estuaries along the Gulf of Guinea in Ghana were also studied for providing data nutrient loading with respect to eutrophication (Biney, 1985). Thus the study on the hydrographical features and the effect of nutrients enrichment is essential in understanding the water as a useful resource, as it gives insight into the benefits to be gained from purposeful management.

1.1. Nutrient behaviour in the estuarine environment

Nitrogen and phosphorus are the two major nutrients taken up by phytoplankton from the water for their healthy growth, apart from siliceous organisms which utilize silicon. The distribution and variation of nutrients in estuarine waters are controlled by the physical, biological and chemical processes taking place in the pertinent environment (Aston, 1980). Because of the local influences from land drainage and often pollution, estuaries are generally enriched in nutrients in comparison to ocean waters. Estuaries may also be considered as natural laboratories where chemical reactions occur during the mixing of river water with seawater, consequently leading to the removal or regeneration of nutrients. The nutrient budget is also influenced by the rate of deposition and resuspension processes of sediments in estuaries.

The behaviour of nutrients during estuarine mixing may vary from one estuary to another and within one estuary it may vary seasonally depending upon environmental conditions. In some estuaries, nutrients exhibit conservative behaviour while in others it is non-conservative. A conservative property is that one where concentration is changed only by physical processes of mixing and dilution and is unaffected by biogeochemical processes (Imberger <u>et</u> <u>al</u>., 1983). Non-conservative property is one where values may be changed as a result of biogeochemical reactions as well as mixing of different water types (Peterson et al., 1975, a and 1975, b; Hobbie et al., 1975). Sharp (1983) suggested that the two types of environments can be considered by using nutrient-salinity plot: (i) low nutrient estuaries that show essentially conservative mixing and (ii) high nutrient estuaries that show variations from conservative to highly non-conservative mixing.

The variation of estuarine chemical constituents with salinity is used to explain the mechanisms like uptake, addition, or conservation of the given constituent within the waterway (Peterson et al., 1978; Callaway & Specht, 1982). Liss (1976) had advocated the usefulness of this concept and Loder & Reichard (1981) proved its application especially when one is cautious about the end member variability. This approach has been used in the study of silicon behaviour in several estuaries (Boyle et al., 1974; Callaway & Specht, 1982; Edmond et al., 1984) and also for other nutrients (Van Bennekom et al., 1978; Sharp et al., 1984).

The speciation of the major nutrients nitrites, nitrates, phosphates and silicates and the transfer of dissolved inorganic form to particulate fraction and vice versa in the aquatic system is complex as a result of biological processes. The important forms of nitrogen involved in the biogeochemical processes in estuaries are the dissolved inorganic species eg. nitrite, nitrate, ammonia and organic nitrogen compounds. The most abundant inorganic form is nitrate which is also the most stable nitrogen species in well oxygenated waters. Van Bennekom et al. (1978) and Fanning & Maynard (1978) have generalized the conservative nitrate behaviour in non-urban tropical estuaries. The nutrient recipient Tamar estuary also exhibited conservative nitrate behaviour (Morris *et al.*, 1981). However, Mackay & Leatherland (1976) and DeSousa *et al.* (1981) have reported that nitrate frequently behaves in a non-conservative manner in Clyde (Scotland) and Mandovi (India) estuaries respectively. Jaworski (1981) has reported the non-conservative behaviour of ammonia in Potomac river estuary.

The productivity of a given estuary depends on two conditions viz. effective regeneration on a rapid time scale and the marine or riverine supply of fresh nitrogenous compounds. During the period of high productivity, it is well known that the assimilation of inorganic nitrogen compounds by primary producers cause to decrease the inorganic form by converting it into dissolved and particulate organic form. The particulate organic form is mostly transported in suspension and rapidly remineralized or may enter into bottom sediments (Rhoads *et al.*, 1975; Nixon and Pilson, 1983). The release of previously deposited nitrogen compounds from estuarine sediments may be a possible source of nutrients for productivity to the overlying waters (Hartwig, 1976). The significance of various factors regulating nitrification and denitrification in estuarine sediments has received considerable attention in recent years (Jenkins & Kemp, 1984). The occurrence of the denitrification processes in organic rich sediments of estuarine zone may induce the adsorption of nitrate from the water column to the sediments (Jorgensen & Sorensen, 1985). N_2 and N_2O produced during this process is transferred to the atmosphere and recycled to the aquatic system (GESAMP, 1987). Ammoniacal nitrogen can often be the next most abundant form of inorganic nitrogen in surface waters where phytoplankton growth has removed a greater part of nitrate-nitrogen.

Phosphorus is a major nutrient regulating the growth and production of phytoplankton and its concentration can be used to predict the total biomass of phytoplankton. The availability of phosphorus to water bodies depends to a large extent on the solubility of phosphorus found in sediments and in suspended inorganic particles. Avnimelech (1983) showed that the reaction between dilute orthophosphate solution and $CaCO_3$ can be attributed to the formation of a calcium carbonate-phosphate complex having a defined solubility behaviour on the control of phosphorus concentration.

On the average, one half of the dissolved phosphorus exists as a soluble inorganic form which may be involved in various dissolution, precipitation or adsorption-desorption reaction (GESAMP, 1987). An equal amount is present as organic phosphorus. Within the estuary there is also a tendancy for phosphorus to be converted to particulate form, by association with iron rich oxide coated mineral particles.

Estuarine sediments are generally rich in phosphorus which may be liberated to overlying waters under favourable conditions and thus have an important effect upon the productivity of these waters. Phosphorus regeneration within the sediments results in creating marked differences of concentration between interstitial and overlying water, leading to the enrichment of the latter by diffusion (Mortimer, 1971). In this connection, phosphorus exchange processes at the sediment-water interface regulated by a variety of mechanisms have been reported by Hayes & Phillips (1958), Pomeroy _et_ _al_. (1965), Harter (1968), Harrison _et_ _al_. (1972) and Nixon (1980).

Pomeroy _et_ _al_. (1965) have attempted by laboratory experiments to measure the release of phosphate from suspended sediments to estuarine waters and have found that a 'buffering' effect was operating the mechanism. Thus, phosphate buffering is of considerable importance when the effects of sewage pollution on estuaries are considered with the role of sediments in releasing phosphorus. A large proportion of inorganic dissolved phosphorus removal occurs in the presence of colloidal iron especially under high pH conditions and in the absence of humic acid (Bale & Morris, 1981; Carpen ter & Smith, 1984).

Silicon has received more attention than the most of the other chemical constituents in estuaries. This is because it is an important nutrient to some marine organisms like diatoms, radiolaria and sponges. Liss (1976) and Aston (1978) have given elaborate reviews of the silicon cycle in estuaries. River borne silicates and glacially weathered particles are the major sources of silicon supply to estuarine environment. In contrast to nitrogen and phosphorus, contribution of dissolved silicon to estuaries from anthropogenic sources are not important relative to glacial weathering.

Silicon is present in river water in three forms: detritus matter, alumino silicates (clay) and dissolved silicon derived from weathering of silicate rocks. During the mixing of river water with seawater in estuaries, increased electrolytic concentration leads to the formation of polymeric form of silicic acid which flocculates and removes the dissolved silicon as alumino silicates (Krauskopf, 1956). This process of removal of silicon in estuaries by flocculation and precipitation depends to a certain extent on the salinity gradient.

In some estuaries the removal of silicon from river water is explainable in terms of simple dilution mechanism (Burton _et_ _al_., 1970 ; Fanning & Pilson, 1973). Milliman & Boyle (1975) have suggested that biological processes are equally important in controlling the concentration and distribution of silicon in estuaries. A study conducted by Kamatani & Takano (1984) suggested that the behaviour of silicon in estuaries is the result of physical, chemical and biological processes which vary from one estuary to another. However, it is very difficult to characterize the silicon behaviour in an estuary especially when the biological processes controlling the growth and population of silica secreting organisms vary so widely and remain undefined.

1.2. The area of study: The Cochin estuary

The Cochin estuary, the largest along the west coast in Kerala State extends between 09°40'N and 10°12'N and 76°10'E and 76°30'E. It has a length of about 70 km and width varies between a few 100 meters to about 6.0 km. It covers approximately an area of 300 km^2. As a shallow semi-enclosed body of water it falls under the category of a tropical positive estuary (Pritchard, 1952). In recent years, this coastal water body had been a centre of intensive survey primarily concentrating on topics of hydrographical parameters and biological production. Hence it was also considered important to obtain information on the range of variations of the nutrient concentration in this estuary.

Since the year 1976, the hydrographic conditions of this estuary had undergone extensive changes by way of (i) interbasin transfer of water from Periyar river to Muvattupuzha river to facilitate a hydroelectric project (ii) construction of a salt water barrier (Thanneermukkam bund) on the southern part of the estuary and (iii) extensive dredging and harbour operations. Apart from these modifications, the estuary is recipient of pollutional discharges necessitating the detailed study of the water body. The status of scientific works conducted is detailed below briefly.

Tides in the Cochin estuary are of mixed semidiurnal type of two successive, high and low water appearing each day with an appreciable difference in range and time (Qasim & Gopinathan, 1969). The maximum frequency of the tide in the years 1969-1970 was observed in the amplitude range of 0.8 to 0.9 m and maximum frequency at 1.1 m (Josanto, 1971). Various environmental features such as temperature, pH, salinity, dissolved oxygen, nutrients, alkalinity and chlorophyll are greatly influenced by the tidal rhythm (Qasim & Gopinathan, 1969). Major changes in the hydrological conditions of Cochin estuary are set about by the tidal currents acting through the barmouth and fresh water discharge into the system during south-west monsoon (Shynamma & Balakrishnan, 1973).

Seasonal changes in temperature are more pronounced on the northern parts of the estuary (25-33°C) than on the southern parts (29-33°C) (Lakshmanan et al., 1982). Warm weather conditions during summer months (premonsoon, Feb-May) registered maximum temperature in this estuary. Thermal stratification is absent during premonsoon period. However, during monsoon months, from the end of May onwards, a sharp thermal gradient develops in this estuary along with changes in pH of the surface waters which has maximum values during pre-monsoon and minimum during monsoon (Silas & Pillai, 1975).

The salinity distribution in this estuary, largely depends upon seawater intrusion and influx of river water. However, the bottom topography and the geographical shape of the estuary complicate the salinity distribution in this estuary. Depending upon the degree of mixing between the fresh water and saltwater, the estuary may vary from a well mixed type to a stratified type. With the onset of monsoon rains, the surface water is considerably diluted by rainfall and a distinct stratification develops with very low saline waters at surface and saltish seawater at the bottom of the Cochin barmouth region (Haridas et al., 1973; Wellershaus, 1971). The Thanneermukkam bund plays a decisive role during all seasons by maintaining the southern parts well mixed at uniform salinity.

Eventhough, considerable work has been done on the hydrography of this estuary, detailed accounts of nutrient distribution and their chemical behaviour are scanty. From the available records nutrient distribution in the Cochin estuary shows a marked seasonal variation which is more pronounced at the surface than at the bottom (Sankaranarayanan & Qasim, 1969; Joseph, 1974). Lakshmanan et al. (1987) have investigated the seasonal distribution of nutrients, the extent of influences from the industrial effluent discharges, urban sewage inputs and agricultural runoff; and also studied the variation of nutrient content with respect to salinity. Variation in nutrient behaviour resulting from interbasin transfer of water and the construction of Thanneermukkam bund has also been reported.

The extent and nature of the saltwater intrusion into the estuarine region during different seasons with respect to varying tidal prisms at the Cochin estuary and its effect in flushing out of pollutants introduced into the system from Periyar industrial belt were studied by Rama Raju et al. (1979).

Study on the sediments of the estuary revealed an admixture of clay, silt and sand terrigenous in nature (Murty & Veerayya, 1981;

Mallik & Suchindan, 1984). The southern part of the estuary was characterised by the coarsest sediments (> 63 µ) and the central portion by clay (< 4 µ). Biogenous material in the form of shells are also located in certain portions of the estuary. It is believed, the present shape and depth of the estuary was controlled to a large extent by the sediments transported by the rivers and may have been modified by the tidal currents acting on the estuary (Mallik & Suchindan, 1984).

The sediments in the estuary may be an important source of phosphorus for promoting aquatic growth and may accelerate eutrophic conditions. Frink (1967) indicated that the sediments can act as a reservoir of nutrients probably capable of supporting the aquatic life for an infinite period of time without additional inputs of nutrients from external sources. In a study conducted by Reddy & Sankaranarayanan (1972) the probable factors influencing the regenerative capacity of muds from the Cochin estuary were reported. The difference in the regenerative property of the muds was attributed to the large variations of nutrient content in the overlying waters.

The distribution of various forms of phosphorus in the sediments of Cochin estuary during different seasons and its exchange between the mud and the overlying waters in relation to the texture of the sediments had been studied by earlier workers (Ansari & Rajagopal, 1974; Murty & Veerayya, 1972). Fine sediments of silt and clay showed higher content of phosphate than coarse sandy sediments.

1.3. Scope of the present study

The nutrient distribution of Cochin estuary had been influenced by the increasing human activities, waste discharges from major industrial establishment on Periyar river banks and from sewage through a net work of the large and small canals. Geographically the region of study plays an important role either directly or indirectly in the livelihood and recreational activity of a large number of inhabitants of the port city. The detrimental effects of pollution affect potable water supply, recreational uses including bathing, fishing etc., agricultural and industrial uses, navigation and preservation of aquatic life.

Eventhough, there are numerous references on hydrographical features of Cochin estuary, very little is known about the physico-chemical parameters, their behaviour, variation with season, interrelationship and processes that control the nutrient chemistry. Furthermore, the nature and chemical composition of the sediments have not so far been clearly established. In order to understand and delineate the nutrient behaviour in the estuary, studies on the various aspects of the physico-chemical parameters of this estuarine environment have been undertaken. Assessing the quality of water and also providing the information on various biogeochemical processes taking place within the estuary would be of added knowledge in the understanding of the above processes.

1.4. Scheme of the work

The work incorporated in this thesis deals with the systematic study of temperature, pH, salinity, dissolved oxygen and nutrients in the Cochin estuary. Fortnightly collections were made from 9 stations (see Fig.1) over a period of one year (June 1985 - May 1986). Results on the texture and grain size analysis, seasonal and spatial variations of interstitial and adsorbed phosphorus in sediments collected

The work is presented in six chapters. Chapter 1 gives the introduction and spells out the aims and scope of the present study. Chapter 2 gives the description of the study area and information on sampling procedures for water and sediment; the various techniques employed for the analyses of the constituents are clearly described.

Chapter 3 presents the hydrographical parameters viz. temperature, pH, salinity and dissolved oxygen. Seasonal and spatial variations of these parameters and interrelationship among them are investigated and discussed.

Chapter 4 is devoted to the studies of the dissolved nitrogen in the estuary. Concentration levels of various dissolved nitrogenous nutrients viz. nitrite, nitrate and ammonia are briefly described. Large variations in the concentration of these constituents are explained on the basis of general hydrographic conditions, discharge of domestic and industrial effluents. Coefficient of correlation and regression between salinity and nitrogenous constituents are worked out.

Chapter 5 deals with the different forms of phosphorus: dissolved inorganic reactive, dissolved organic, particulate reactive and total reactive phosphorus concentrations both at surface and bottom waters are included. Factors leading to the variations in concentrations are examined in detail. Seasonal and spatial variations of interstitial and adsorbed phosphorus in the sediments are discussed in relation to the textural characteristics of the sediment and hydrographical parameters like pH, salinity and dissolved oxygen and reactive phosphorus of overlying waters. The various factors affecting the adsorption/desorption mechanism of these constituents between overlying

Chapter 6 describes the chemical behaviour of dissolved silicon in the estuary.

The results and salient features of the studies conducted are summarised, followed by a list of references. The values of the various parameters measured are given in tables, which are appended at the end, while the corresponding figures are incorporated in the text itself. Representative seasonal distributions are also presented at the end.

CHAPTER 2

MATERIALS AND METHODS

A brief description of the Cochin estuarine system and an outline of the methods employed in the present study are given in this chapter.

2.1. Description of location

The Cochin estuarine system (09°40'-10°12' N; 76°10' - 76°30'E) is connected to the sea through a permanent opening, the barmouth at Cochin and two seasonal openings during monsoon (Jun.-Sep.) period: one at Andhakaranazhi and another at Azhikode (Fig.1). The Cochin barmouth is 450m wide, dredged to a depth of 10-13m through which tides act within the estuary. Cochin is the major port on the South West Coast of India.

Two major rivers discharge fresh water into the estuarine system; the Periyar flows into the northern parts and Muvattupuzha into the southern parts of the estuary. A large number of heavy industrial units are situated on the Periyar river. The saline water intrusion to the southern parts of the estuary is regulated by Thanneermukkam bund, a salt water barrier commissioned in 1975. Four rivers namely Achankovil, Meenachil,Manimala and Pamba discharge

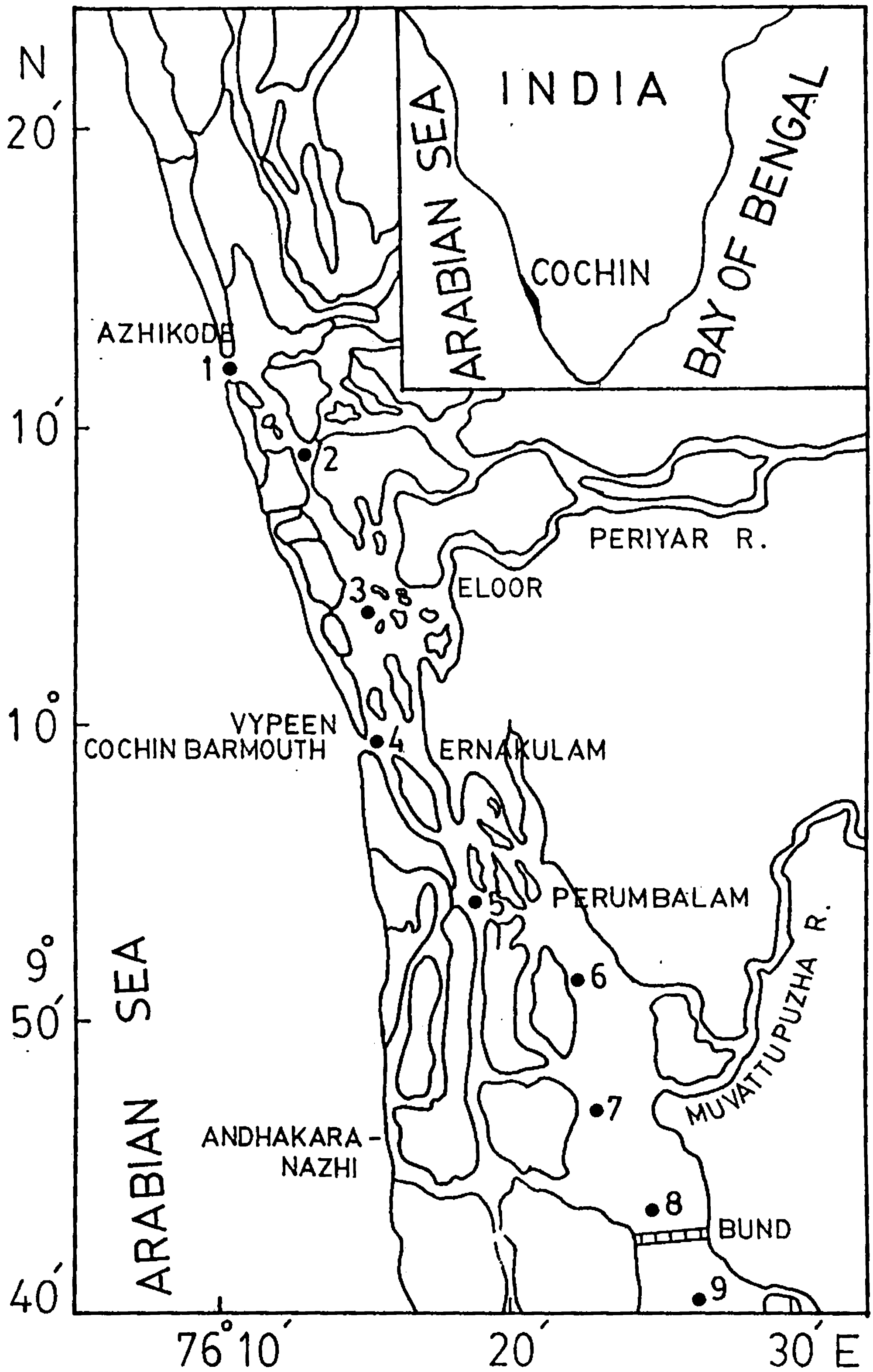

Fig. 1. Map of Cochin estuary showing location of stations.

The depth of the estuary varies moderately. Most of the area is around 3m deep, but the shipping channel at Cochin harbour area is periodically dredged to a depth of about 13m. The region, south of barmouth gradually becomes shallower from a depth of 7m at Perumbalam to about 3.5m at Thanneermukkam during monsoon. The tides in the Cochin estuary are of mixed semi-diurnal type with an average range of about 90cm. During the flood tide the seawater enters the estuary via Cochin barmouth and the flow reverses during the ebb-tide. The magnitude of influence of the tide progressively decreases with increasing distances from the barmouth and reaches almost upto Perumbavoor (about 35 km upstream) along the Periyar river.

The Cochin harbour has attained strategic importance because of its commercial prominence as well as defence needs; it houses a large oil tanker berth, a conveyor belt system for fertilizer transfer and a major ship building yard.

2.2. Analytical techniques

2.2.1. Sampling procedure

Location map (Fig.1) indicates the area of investigation and location of sampling stations (1-9). The stations were so fixed as to give a fairly good coverage of the prevailing complex environmental conditions. Surface and bottom water samples from these stations were collected at fortnightly intervals from June 1985 to May 1986. Surface samples were collected using a clean plastic bucket and bottom water (0.5m above floor) was drawn by using a modified Hytech water sampler. Samples for nutrient analysis were collected in precleaned polythene bottles and stored deep frozen. The surficial sediment samples were collected using a van Veen grab (area $0.032m^2$). The samples were taken in polythene bags and stored deep frozen.

2.2.2. Methods

Temperature was measured with a sensitive thermometer (1/10°C). pH measurements were made using a portable Elico pH meter. Methods described in Strickland & Parsons (1977) were adopted for the estimation of salinity and dissolved oxygen. Nitrite-nitrogen was determined as proposed by Bendschneider & Robinson (1952) method suggested in Strickland & Parsons (1977). Nitrate-nitrogen was estimated by the method originally proposed by Mullin & Riley (1955) and later modified by Grasshoff (1983). The indophenol blue method was adopted for the determination of ammonia in water samples (Koroleff, 1983, a).

The scheme of fractionation and estimation of the four forms of phosphorus given by Strickland & Parsons (1977) was followed.

Inorganic reactive phosphorus (IRP) was estimated spectrophotometrically by the method of Murphy & Riley (1962). Total reactive phosphorus (TRP) (dissolved) was estimated by converting organically bound phosphate into reactive (ortho) phosphate by the oxidation with peroxydisulphate and sulphuric acid (Koroleff, 1983, b). The resulting orthophosphate was then determined by the procedure described under inorganic reactive phosphorus. Dissolved organic phosphorus (DOP) of the sample was obtained by subtracting inorganic reactive phosphorus (IRP) from total reactive phosphorus (TRP); (DOP = TRP -IRP). Particulate reactive phosphorus (PRP) of the samples were estimated by subtracting the value of the inorganic reactive phosphorus (filtered) from the inorganic reactive phosphorus (unfiltered). Details on the definitions and determinations of the various forms of phosphates are given on pages 45-47 of "A Practical Handbook of Seawater Analysis" by Strickland & Parsons (1977).

Reactive silicate-silicon was determined by the method suggested by Koroleff (1983, c) which involves the use of ascorbic acid as the reductant. In this method only straight chain polymers containing less than four silicic acid ($Si(OH)_4$) units react with molybdate solution.

Textural analysis of the sediment was carried out by drying the samples in a hot air oven (90°C) for 6 hr and subsequent mechanical sieving and pipette analysis as described by Krumbein & Pettijohn (1938). Shepard's nomenclature (Shepard, 1954) was used to describe the texture.

Phosphorus content in sediments as interstitial (NaCl leached) and adsorbed (NaOH leached) phosphorus was estimated by the scheme proposed by Rochford (1951),but employing the mixed reagent suggested by Strickland & Parsons (1977); the results are expressed as µg at PO_4^{3-}-P g^{-1} of wet mud.

All chemicals used were of analytical reagent grade. Ammonia-free water was prepared by redistilling distilled water treated with potassium peroxydisulphate (1 gm l^{-1}) and sodium hydroxide (15ml of 0.5 N l^{-1}). Hitachi Model 200-20 uv - visible spectrophotometer was used for photometric measurements.

The results are analysed and presented for three distinct seasons namely (i) monsoon (Jun.-Sep.) (ii) postmonsoon (Oct.-Jan.) and (iii) premonsoon (Feb.-May) prevailing in the region.

CHAPTER 3

HYDROGRAPHY

The study of the hydrographical parameters of the estuarine environment is of great importance while attempting to characterise the general features, distribution pattern and relative abundance of nutrients. Equally significant are these studies with regard to pollution control, harbour design, marine traffic routing etc. The hydrographical conditions in an estuary mainly depend on the intrusion of seawater associated with tides and influx of fresh water from rivers. The precipitation/evaporation processes also have profound effects on the hydrographical changes. In addition to these factors, the bottom topography and the geographical shape of an estuary have added influence on the hydrographical conditions in the estuary.

The hydrography of the Cochin estuary has been investigated by several workers (Ramamirtham & Jayaraman,1963; George & Kartha, 1963; Qasim & Reddy, 1967; Qasim _et al._, 1968; Sankaranarayanan & Qasim, 1969; Josanto, 1971; Wellershaus, 1971; Haridas _et al._, 1973; Shynamma & Balakrishnan, 1973; Manikoth & Salih, 1974, Joseph, 1974; Lakshmanan _et al._, 1982; Sankaranarayanan _et al._, 1986). The information available includes seasonal distribution of temperature, salinity, dissolved oxygen, pH, alkalinity and nutrients of the region as a whole or part. In recent years, the Cochin estuary has been a centre of intense activities with regard to hydrological changes and it was considered important to obtain more and detailed information on the range of variation and distribution of the hydrographical features. The present study on the hydrography attempts to elucidate data on the seasonal and spatial distribution of temperature, pH, salinity and dissolved oxygen for the period of survey (June 1985 to May 1986); the methods of sampling and analysis are given in Chapter 2.

3.1. Temperature

The distribution of temperature in an estuary is dependent on the mixing of inflowing river water and tidally influenced seawater; processess like exchange of heat with atmosphere and any localised phenomena are also likely to influence the distribution.

Temperature at surface and bottom at different locations during the period of survey are given in Table 1. Distribution and seasonal variation of temperature at surface and bottom are represented by drawing isolines as chart of stations versus time (Fig.2). Temperature varies from low values of 25.3°C at surface and bottom during August, 1985 to high values of 33.4°C at surface and 32.6°C at bottom both during April 1986. The low monsoonal values increase gradually and reach maximum values during the premonsoon period. Seasonal variation of temperature at surface was less pronounced in the southern part of the estuary (25.3° - 30.7°C) between stns. 6 and 9 than on the northern parts (25.3° - 33.4°C) between stns. 1 and 4. The seasonal variation of bottom temperature which was nearly similar to that at surface is mainly due to the climatic setting for this tropical region. The observed low monsoonal values in the barmouth region may be

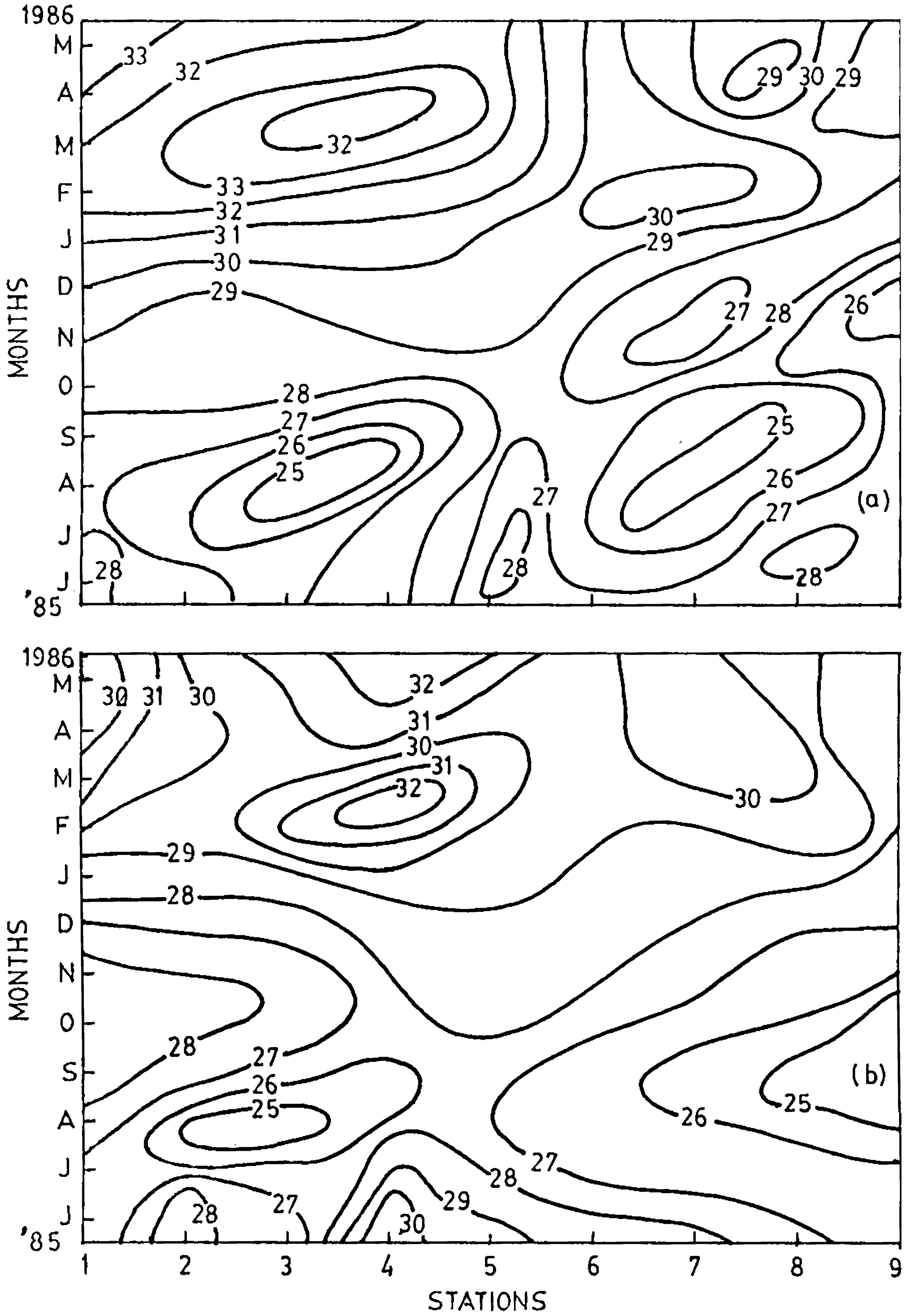

Fig.2. Time Series curve of temperature (°C) at surface (a) and bottom (b)

and intrusion of cold saline water from Arabian sea into the deeper layers of barmouth region. This feature had also been observed by earlier workers (Ramamirtham & Jayaraman, 1963; Sankaranarayanan & Qasim, 1969).

The northern parts of the estuary exhibited slightly higher temperatures compared to the southern parts giving rise to horizontal gradients,more pronounced in April (The difference in temperature is about 4.0°C). Relatively the higher temperatures recorded on the northern parts of the estuary may be partly due to low influx of fresh water from Periyar river during premonsoon, while in the southern parts large amount of colder river waters ($\simeq$ 27°C) flow into the region. Stn. 2 located on the northern part registered the maximum value of temperature difference, 3°C between surface and bottom waters during March 1986 giving rise to pronounced vertical gradient.

The formation of such vertical gradients have been observed by Lakshmanan *et al*. (1982) in the lower reaches of Periyar. The present investigations bring out the presence of such a phenomenon not only in the lower reaches of Periyar but also extending to the other parts of the northern arms of the estuary.

3.2. Salinity

Salinity has been recognised as the parameter in studying the mixing processes and intrusion of saline waters into estuaries by tidal action. The mixing and diffusion phenomena occurring in estuaries are largely influenced by salinity distribution pattern. In estuaries wide fluctuations in salinity are generally observed, usually lower than seawater, but in regions with high evaporation and little rainfall estuarine salinity level may exceed 35×10^{-3}.

Results on salinity at surface and bottom at stns. 1-9 during the period of survey are given in Table 2; time series curves of surface and bottom salinity of these stations are given in Fig. 3.

The Cochin estuarine system was largely influenced by the influx of freshwater from rivers and intrusion of seawater into the estuary via the barmouth. In the northern region along stns. 1 to 4 during monsoon, low salinity values varying between 7 and 12 x 10^{-3} at the surface and higher values ranging from 15 to 27 x 10^{-3} at the bottom were encountered. The high vertical salinity gradient at Cochin barmouth region indicates a distinct stratification during this period. Sankaranarayanan et al. (1986) also found that stratification develops at the mouth of the estuary, when large volumes of freshwater flow into the estuary. A gradual increase in salinity could be observed as the season progresses to postmonsoon and premonsoon. The highest value (35 x 10^{-3}) was recorded at surface and bottom of stns. 1 to 4 during premonsoon. This was mainly due to the intrusion of seawater through the barmouth. It was also observed that during premonsoon the vertical salinity gradient tend to be minimal.

In the southern region, along stns. 5 to 9 low values of salinity ranging between 0 to 10 x 10^{-3} at surface and 0 to 12 x 10^{-3} at bottom were observed during monsoon. This was brought about by the combined effect of land drainage from the prevailing monsoonal rains causing high freshwater discharge from the river and the intrusion of salt water. Fresh water conditions were observed at surface at stns. 8 and 9 during monsoon. As the season advances to postmonsoon and premonsoon higher values ranging from 10 to 22 x 10^{-3} at surface and 12 to 24 x 10^{-3} at bottom were observed.

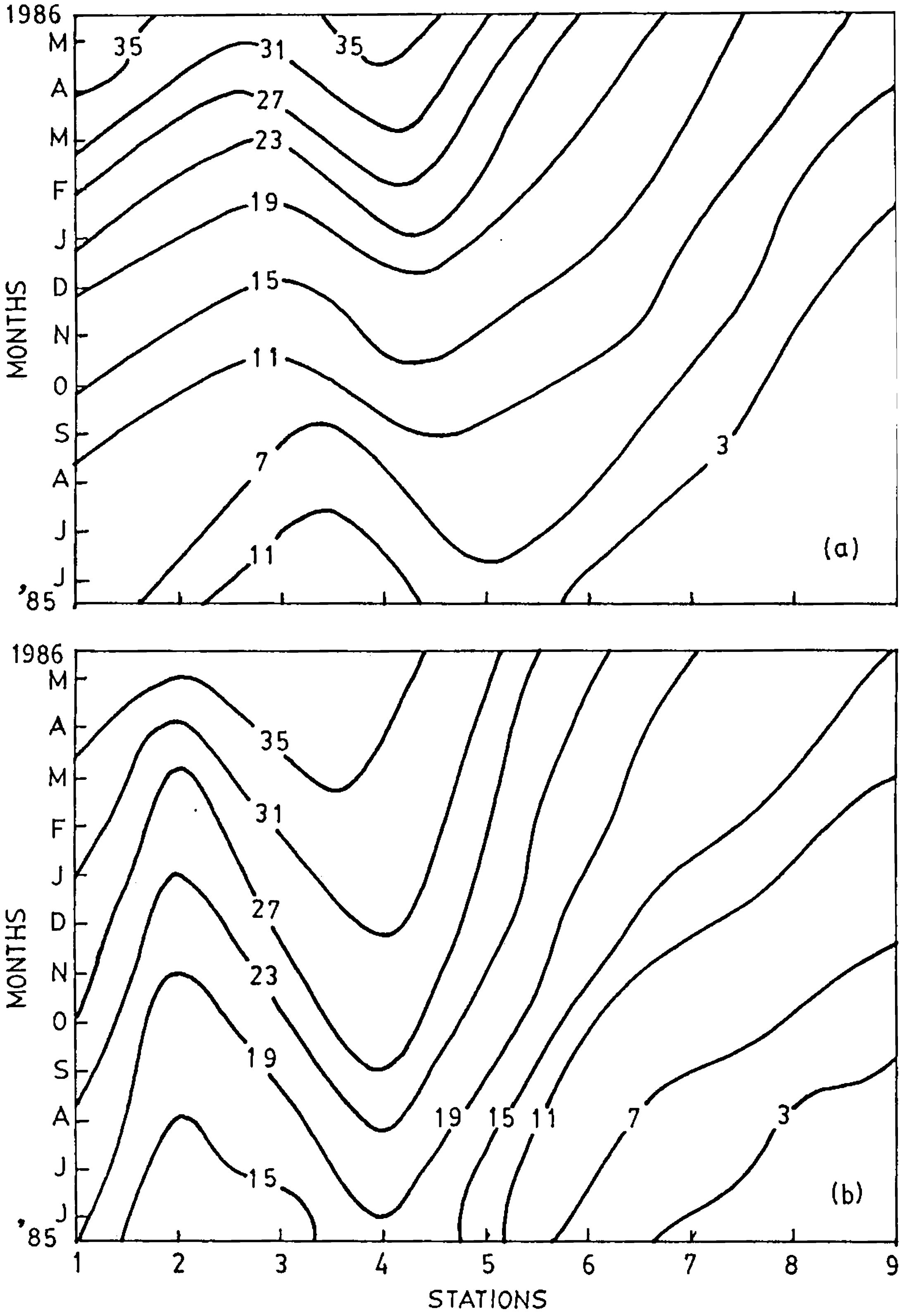

Fig. 3. Time series curve of salinity $(\times 10^{-3})$ at surface (a) and bottom (b).

and low discharge of freshwater into the estuary. The vertical salinity gradient is minimum in the southern region during all seasons.

Time series curves of bottom salinity at the northern region of the estuary indicate that the effect of seawater influx through stn.1 (Azhikode outlet) has a significant influence on the hydrography upto stn. 2. However, the effect of seawater influx through stn.4 (Cochin barmouth) was more pronounced and covers a large area between stns. 2 and 4 which is evidenced by the pattern of the isohaline contour distribution at stns. 2-4 (Fig. 3b). Hence the net effect of seawater intrusion on the hydrography of the northern regions are largely influenced by the influx of seawater through stn. 4 than from stn. 1. When comparing the bottom distribution to that at surface, an added feature was the freshwater dilution occurring between stns. 2 and 3 evidenced by the vertically inclined isohaline pattern along the longitudinal section between the two stations.

Eventhough, influx of large amount of freshwater occurs between stns. 7 and 8, the dilution of seawater was not as pronounced as that observed on the northern regions. This is due to the nature of the semi-enclosed waterway by the construction of Thanneermukkam bund on the southern side of the estuary. The stationwise salinity variation for a given time interval at surface was significant, the changes at the bottom being very sharp.

3.3. Dilution of seawater

Fractional estimates on freshwater content in estuaries can be applied for the determination of dilution of seawater. Bowden(1980) suggested that the amount of freshwater removed by flushing is the same as that is being added by river discharge. The important processes which bring freshwater to the estuarine system are land runoff, precipitation and river discharge.

The amount of freshwater present at any given location in an estuary in terms of salinity (10^{-3}) of the same location can be formulated as $F = 1 - \frac{S1}{S2}$

Where F is the fraction of freshwater in the sample, S_1 is the salinity of the sample collected from the location inside the estuary and S_2 is the salinity of the coastal water (Officer, 1976). Fig. 4 gives the surface and bottom freshwater fractional values as plotted against the stations for the three seasons.

The northern part of the estuary exhibits wide seasonal variation in freshwater content both at surface and bottom. During monsoon stn.1 traced a value of 0.47 at surface and 0.25 at bottom. With the advent of postmonsoon, values gradually decreased and during premonsoon the waterway turned to near saline conditions (fraction value 0.01). Generally bottom values at all stations are lower than surface values for all seasons.

A significant feature is that during premonsoon, bottom layers denoting saline water conditions prevailed over the entire bottom region of the northern parts of the estuary ($F \simeq 0.01$). This gives rise to stratification with surface layers containing higher freshwater fractions in the northern parts during premonsoon.

Equally significant are the features on the southern regions where both surface and bottom layers trace nearly the same values for freshwater fractional distribution indicating a well mixed zone in these parts of the estuary.

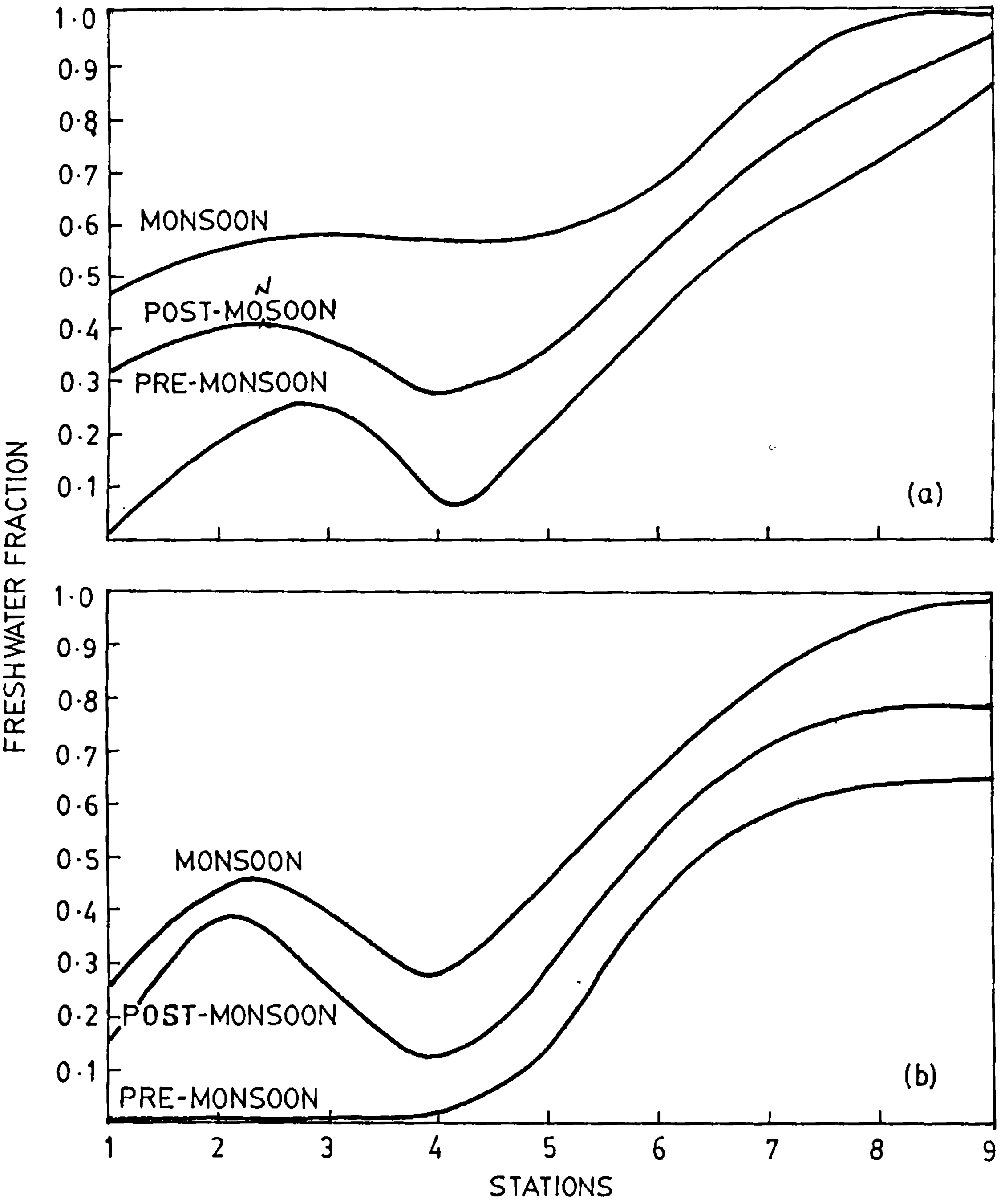

Fig. 4. Seasonal distribution of freshwater fraction at surface (a) and bottom (b).

3.4. pH

Many of the life processes are dependent on and are sensitive to the hydrogen ion concentration in the surrounding medium. The pH of a medium depends on many factors like photosynthetic activity, rainfall, nature of dissolved materials, discharge of effluents, sewage into it etc. Variation in pH due to chemical and other industrial discharges renders a stream unsuitable not only for recreational purposes but also for the rearing of fish and other aquatic life (Webb, 1982). George (1979) has stated that the tolerance range for most biological organisms is quite narrow and critical. Low values of pH may cause rapid corrosion of hulls of ships whereas high values bring about incrustation and brittleness to pipes. Significantly, close monitoring of pH value for acidic or alkaline discharges enable to identify zones of pollution and other quality conditions for use of water (Clark _et al._, 1977).

Data on pH of Cochin estuary are given in Table 3. Distribution pattern of pH at surface and bottom waters at all stations during the period of survey as time series curves is given as Fig. 5. The range of values varies from 6.6 at surface of stns. 8 and 9 to 8.2 at surface of stns. 3 and 4. It is also evident from the figure that pronounced seasonal variations are observed in pH distribution. Natural pH values are traced during monsoon month, at surface when freshwater influx occurs. The pH increases seasonally up to postmonsoon period. The maximum value of pH was recorded at surface during postmonsoon in the barmouth region. This is attributed to the near marine condition and the excessive photosynthetic activity of algae, which results in depletion of the amount of CO_2 and hence

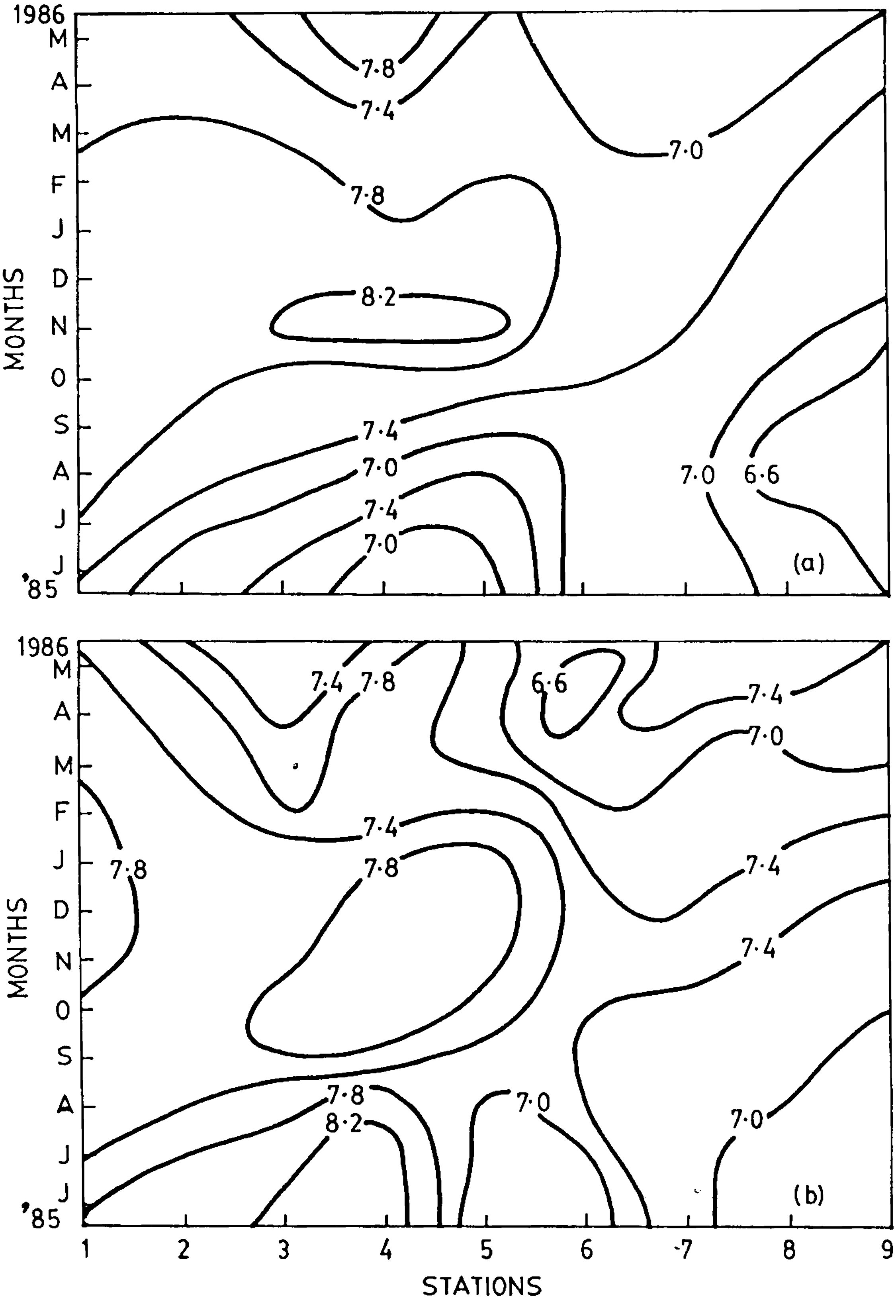

Fig. 5. Time series curve of pH at surface (a) and bottom (b).

increase of pH value. The high phytoplanktonic production during postmonsoon in Cochin backwaters was recorded by earlier workers (Silas & Pillai, 1975; Nair et al., 1975). With the onset of monsoon rapid variation was observed in the vertical at the barmouth region (stns. 3 and 4 - pH 7.1 - 8.2; 7.0 - 8.2 respectively).

The northern region recorded higher pH values than the southern region throughout the period of survey. It is also significant that the values gradually decrease from the barmouth region to the southern tip of the estuary. This may be due to the reduced influence of the seawater intrusion. In the northern region the value ranged from 7.0 to 8.0 at surface and 7.4 to 8.2 at bottom during monsoon. The values at the bottom are higher than those at the surface. This significant vertical gradient at barmouth region is due to the combined effect of the influx of low pH freshwater at surface and intrusion of high pH saline water through the Cochin barmouth at the bottom.

The difference in variation of pH between surface and bottom in the northern region during postmonsoon and premonsoon is not well defined. In the southern region the values ranged from 6.6 to 8.2 at surface and 7.0 to 8.0 at bottom.

3.5. Dissolved Oxygen

Dissolved oxygen (DO) is an important water quality parameter in assessing water pollution. Though atmospheric oxygen is abundant, its solubility in water is low 9.94 ml l^{-1} at 1°C, and 5.28 ml l^{-1} at 30°C in freshwater and 7.97 ml l^{-1} at 1°C and 4.41 ml l^{-1} at 30°C in seawater of salinity 33 x 10^{-3} (Riley & Chester, 1971,a). The depletion of oxygen content leads to undesirable obnoxious odours under anaerobic conditions (Doudoroff Shumway & Peter, 1970; Nelson, 1978), The concentration and distribution of oxygen in natural waters depend on various factors such as temperature, partial pressure of the gas in the atmosphere and salinity. Chemical behaviour (Schroeder, 1980) and rate of depletion of oxygen (Wahby et al., 1978) have been used to investigate the quality of water bodies. Studies on salinity dependent oxygen solubility may help to elucidate the various physical, chemical, and biological processes taking place in estuarine waters (DeSousa & Sen Gupta, 1986).

Results of DO at surface and bottom at all stations are given in Table 4. Distribution pattern of DO at surface and bottom as time series curves is represented in Fig. 6. Both seasonal and spatial variations are again well reflected in the DO patterns. On the northern regions DO values range from 4.75 to 6.56 ml l^{-1} at surface and 4.71 to 5.86 ml l^{-1} at the bottom during monsoon. The values decreased as the season advanced to postmonsoon and premonsoon. The premonsoonal values vary between 4.06 to 6.13 ml l^{-1} at surface and 3.07 to 4.71 ml l^{-1} at bottom. The lowest values (3.07 - 3.23 ml l^{-1}) were recorded along stns. 2 and 3 during premonsoon; this may be interpreted as the combined effect of low solubility of oxygen in high saline waters (31 - 34 x 10^{-3}) and waste discharged from fishing industries located on the northern parts.

Higher oxygen values were observed on the southern parts of the estuary. The high monsoonal values (7.07 to 8.50 ml l^{-1}) at the surface along stns. 6 to 9 gradually decrease during premonsoon (6.98 - 7.73 ml l^{-1}). Relatively higher values observed at the southern region as compared to the northern region may be due to the higher solubility of oxygen in less saline waters. High values

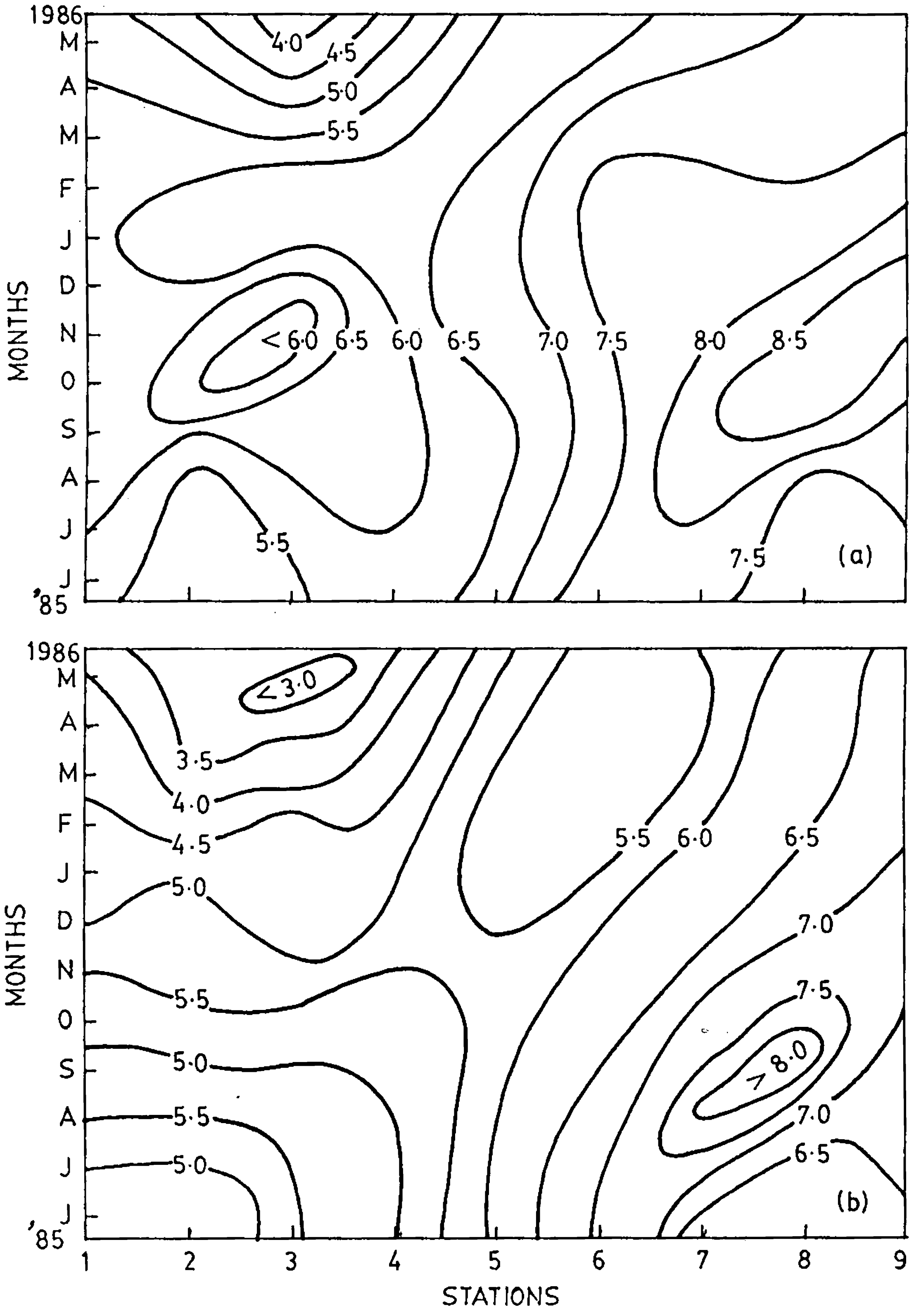

Fig. 6. Time series curve of dissolved oxygen (ml l^{-1}) at surface (a) and bottom (b).

of DO in the southern regions during monsoon with the low saline content and lower values of DO in the northern regions during premonsoon with high saline water signify the solubility process

Thus, the salient features of the study may be summarized as given below.

The net effect of varying amount of lighter freshwater flowing from Periyar river over the heavier seawater from Arabian sea intruding into the deeper layers of barmouth region during different seasons causes to exhibit a pronounced seasonal and spatial variation of temperature and salinity in the northern part of the estuary. A pronounced vertical salinity gradient thus develops at Cochin barmouth region during monsoon. During non-monsoonal months this region becomes more or less homogeneous. For the corresponding periods, the southern parts of the estuary is observed as well mixed. Lower values of salinity in the southern regions is due to the combined effect of land drainage from the prevailing monsoonal rains causing high freshwater discharge from the rivers and relatively weak intrusion of salt water.

A pronounced seasonal variation of pH is observed with higher values during postmonsoon which may be attributed partly to marine conditions and partly to the excessive photosynthetic activity of algae. The influx of low pH fresh water at surface and intrusion of high pH saline waters through the Cochin barmouth along the bottom layers is a significant factor regulating the pH values in the estuary.

Again, both seasonal and spatial variation of DO is observed; during premonsoon low DO is observed as a result of the low solubility of oxygen in high saline water and waste discharge from fishing industries located on the northern parts. High DO is observed during

CHAPTER 4

NITROGEN IN THE ESTUARY

Nitrogen is one of the important nutrients for phytoplankton growth in the marine environment (Ryther & Dunstan, 1971; Thayer, 1974). Hunter (1970) suggested that food resources with a C:N ratio (by weight) greater than 17:1 are nitrogen poor and will inhibit heterotrophic growth. Because of the importance of nitrogen in regulating primary production, numerous investigators have followed the seasonal changes in the concentration of nitrogen species in relation to phytoplankton biomass and/or production (Eppley *et al.*, 1973; McCarthy *et al.*, 1977; Solorzano & Ehrlich, 1977; DeSousa *et al.*, 1981; Qasim & Sen Gupta, 1981; Sharp, 1983).

The hydrosphere contains about $23x10^{12}$ tons of dissolved molecular nitrogen (an amount which represents only 0.5% of the global nitrogen budget). Of the soluble combined nitrogen, 65% is present as nitrate and nitrite (Martin, 1970). A comprehensive nitrogen budget has been proposed by Van Bennekom & Salomons (1981) who present data on a dozen major rivers including some highly polluted ones.

Nitrogen exists in nine oxidation states (-3 to +5)all of which have significant roles in the marine environment (Martin, 1970). The processes controlling the distribution of various forms of nitrogen between coastal water, estuarine waters and nearshore shelf waters are, however, not well understood. The concentration of various forms of nitrogen in an estuary at a given time is the resultant of input rates, the interconversion reactions occurring within the water column and the rate of loss by way of outflow, denitrification and sediment associated deposition. Essentially, three major processes bring nitrogen to the sea (1) volcanic activity (ii) atmospheric precipitation and (iii) continental drainage. Three processes remove nitrogen from the sea (i) loss to deep marine sediments, (ii) migration of marine animals and (iii) loss of nitrogen to the atmosphere (Martin, 1970); photosynthetic activity in the euphotic zone also removes nitrogen.

Examination of the variations in concentration of nitrogen species in time and space will provide an insight into some of the above processes controlling the distribution of nitrogen in the estuarine ecosystems. Such studies on the distribution and flux of nitrogen in estuarine ecosystems were carried out at Pamlico river estuary (Hobbie _et al_., 1975), Clyde estuary (Mackay & Leatherland 1976), Mississippi river estuary (Ho & Barrett 1977), Tamar estuary (Morris _et al_., 1981) and Delaware estuary (Sharp _et al_., 1982).

The important forms of combined nitrogen are the dissolved inorganic species eg. nitrite, nitrate and ammonia, dissolved organic nitrogen and particulate (inorganic/organic) nitrogen. By a series of biogeochemical reactions all these forms of nitrogen are interrelated, known as the 'nitrogen cycle'. The features and mechanisms of nitrogen cycle are generally influenced by human activitiy and the cycle is no longer at a steady state. The recent observation on 'new' nitrogen as an estuarine nutrient serves to illustrate the productivity which may depend on such extreme conditions of very effective regeneration in rapid time scales. Of the above species, the behaviour and fate of inorganic nitrogen compounds are here under discussed briefly.

Nitrite-nitrogen is an intermediate state of nitrogen in the oxidation of ammonia to nitrate and in the reduction of nitrate. Nitrites can enter the aquatic system through effluents from industries using it as a corrosion inhibitor (Owens, 1978); certain biologically purified wastes may also contain large amounts of nitrite. Excessive concentration of nitrite may be indicative of water pollution. Nitrite may be assimilated by phytoplankton especially during the period of luxury feeding; surplus of nitrite stimulates planktonic bloom (Martin, 1968). The effect of acute nitrite exposure to the cray fish was studied by Gutzmer & Tomasso (1985); continued intake of nitrite by fish can lead to hypoxia and cyanosis (Lewis & Morris, 1986). Nitrite poisioning frequently observed in fish is called brown blood disease (Boyd & Pillai, 1984).

The release of previously deposited nitrogen compounds from the estuarine sediments may be a possible source of nitrite to overlying waters. Organic nitrogen regenerated from the sediments is brought to the overlying waters by diffusion or by churning of the media. Natural level of nitrite in estuarine waters range between 0.5 and 6.0 µg at N l^{-1} and is usually very high when compared to the seawater concentration ($<$0.1µg at N l^{-1}). However, Sarala Devi _et al_. (1983) have reported very low nitrite concentration values for selected estuaries of Kerala which ranged between 0.05 to 2.16 µg at l^{-1} (Table 5).

Nitrate is an essential nutrient for the growth of many photosynthetic autotrophs and has been identified as the growth limiting nutrient. Generally appreciable amounts of nitrate are present in surface waters except when intensive growth of phytoplankton occurs. Nitrate is considered to be the only thermodynamically stable oxidation level of nitrogen in the presence of oxygen in seawater (Sillen,1961). Many estuaries receive considerable quantities of anthropogenic nitrogen, usually in the form of nitrate, derived largely from land drainage, from agricultural run off, and application of nitrogenous fertilizers (Cole & Gessel, 1965). The river water concentration of nitrates entering estuaries by human activities may however, be several times greater than the average world wide values for river water. Natural level of nitrate in most estuarine waters range between 10.0 and 40.0 µg at N l^{-1} (Sharp, 1983); however, in certain estuaries (Tamar estuary, Scheldt estuary, Potomac river estuary) reported values are in excess of 100 µg at N l^{-1}. Meybeck (1982) has computed the weighted average nitrate concentration as 100 µg at N l^{-1} based on world wide river data. High concentration of nitrate is harmful to children and may cause the illness known as infant methemoglobinemia (Banoub, 1980). A limit of 10 mg l^{-1} nitrate ($\simeq$ 161.3 µg at N l^{-1}) has been imposed as the upper limit in drinking waters to prevent this disorder (Rand et al., 1976).

In estuaries nitrate is removed through biological utilization and denitrification. DeSousa et al. (1981) suggested that nitrate loss due to denitrification could be ruled out in shallow and well oxygenated estuaries. Hill (1979) recognized the possibility that denitrification in silt/mud sediment may result in loss of nitrate from stream waters despite the fact that the water is well oxygenated; O'Neill &

Holding (1975) inferred that such denitrification is dependent upon the concentration of nitrate in overlying waters and logarithmically related to the concentration of nitrate reducing bacteria.

Nitrite and nitrate are not the only forms of nitrogen that can be used by marine plants to satisfy their nutrient needs for growth; other nutritional forms of nitrogen include ammonia, urea, and amino acids. Ammonia is the first inorganic product in the regeneration of nitrogen. Ammonia occurs in two forms, unionised ammonia and ammonium ion, in a pH and temperature dependent equilibrium.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

As pH rises, concentration of unionised ammonia (NH_3) increases relative to ammonium ion. The effect of increase of temperature is less than that of increase of pH on this equilibrium. Natural waters always contain a small amount of ammonia nitrogen as a result of the natural biochemical process; the relative concentrations depend on pH and temperature of the media.

The transformation of inorganic nitrogen into organic nitrogen occurs through the photosynthetic growth of aquatic plants. The reverse of this process results in the formation of ammonia from organic matter by a complex mechanism involving cell autolysis and microorganisms. Ammonia can be lost from water column by volatilization but oxidation results in nitrification mainly by microorganism, and produces nitrate which is non-volatile.

Among the compounds of nitrogen, ammonia has been shown to be preferred for planktonic assimilation; it also inhibits the utilization of other forms such as nitrite and nitrate in its presence (Conway, 1977; McCarthy et al., 1977). According to Dugan (1975) ammonia can be combined biochemically to form amino acids which can then be converted to a variety of other organic nitrogen forms; this aspect is termed as 'organic loop' in the nitrogen cycle.

Fisher et al. (1982) considered recycled nitrogen via ammonia to be a major food source for primary producers. The general range of values for ammonia from selected estuaries of Kerala (Table 5) are 3 to 15 µg at l^{-1}. Evidently an increase in concentration of ammonia in estuarine water is observed when aquatic organisms are dying off.

4.1. Nitrogen cycling in the aquatic environment

The biogeochemically controlled nitrogen cycle in the estuarine environment is unusually complex involving a large number of nitrogen species, varying from its reduced form (NH_3) to the highly oxidised form (NO_3^-). The behaviour and chemical transformation of nitrogen species in the estuarine environment is influenced by the riverine transport of nitrogen compounds from fresh water sources and biological activity and ultimately results in its removal to the sea. To evaluate the interactions and effects of human activities on the estuarine nitrogen cycle, it is necessary to first compare the nitrogen cycling in the adjacent ecosystems of the aquatic environment. Fig. 7 provides schematic representation of nitrogen cycle in the riverine media, estuarine waters and the sea.

Common to the three sub-systems, atmospheric nitrogen is converted to inorganic/organic dissolved nitrogen by nitrogen fixing

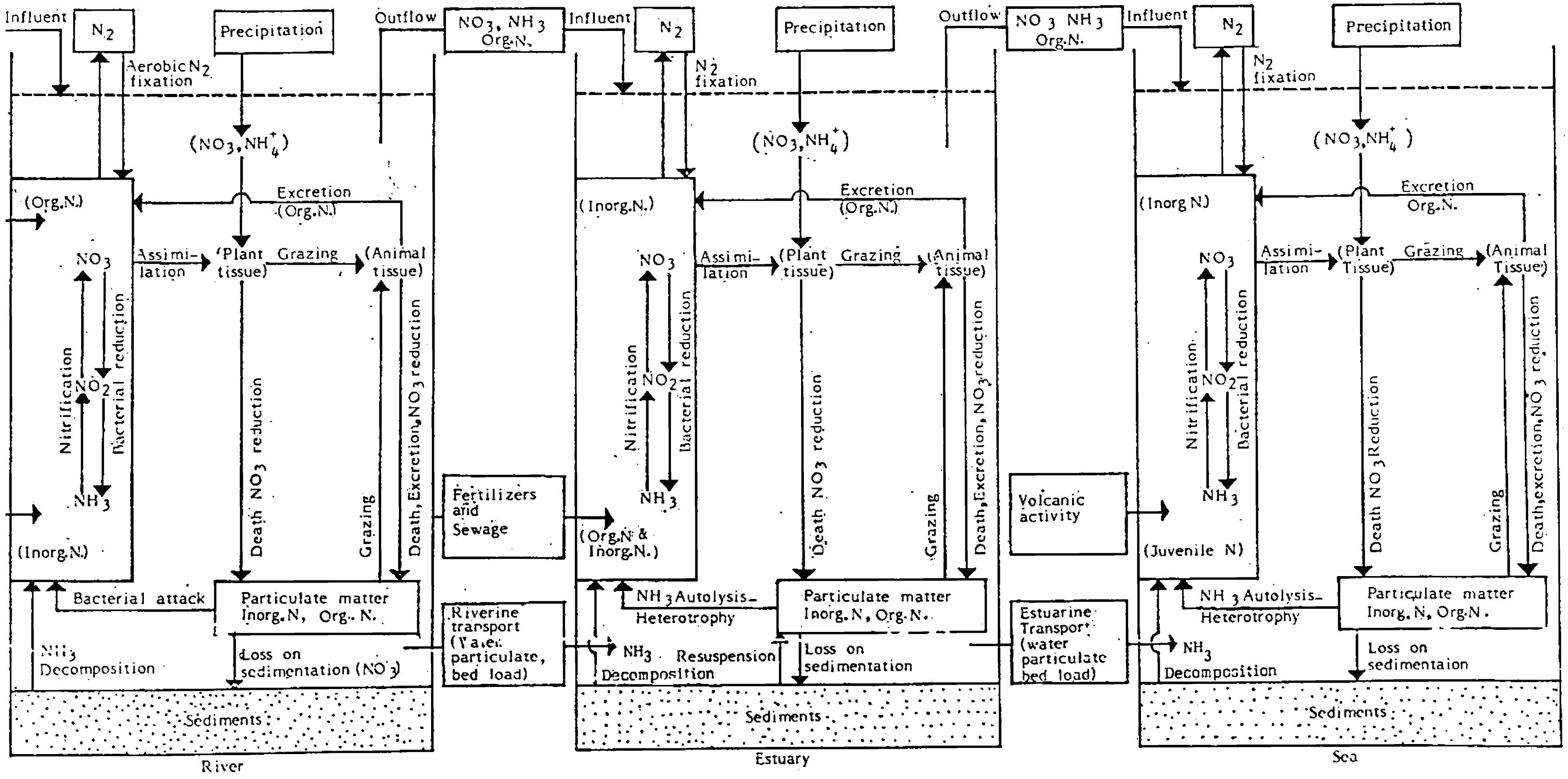

Fig. 7. General scheme of nitrogen cycling in the aquatic environment.

bacteria; contribution from precipitation (rainfall and atmospheric particulates) also accounts for part of the transfer. Basically, in all the three environments, plant assimilation of the nitrogenous nutrients is subsequently followed by grazing in which inorganic nitrogen forms are transformed to organic compounds by animals. Organic nitrogen found in the excreta of animals is a contributing factor to the total nitrogen content in each of the media. Additionally, the particulate matter formed on death of animals is acted upon by bacteria to be returned to the nitrogen pool for further cycling. Part of the particulate matter is sedimented; thereupon bacterial action/leaching causes return of nitrogen principally as ammonia to the overlying waters. Land drainage and ground water also supply inorganic/organic nitrogen to the river waters. In the case of estuaries the 'newer' nitrogen sources are the effluents from the industrial units (mainly fertilizer plants) and disposed sewage often found to be in substantial amounts. Yet another contributing source to the sea, would be the juvenile nitrogen entering via volcanic activities. The freshwater bodies (rivers) and estuaries also experience loss of nitrogen by way of outflow.

Though nitrogen cycling is of a complex nature, characterization of its cycling in the riverine, estuarine and oceanic waters help to identify the potential sources, major pathways of losses as well as internal processes. Hence in the most simplified form, nitrogen is transported by riverine waters, particulates, and bed loads to the estuary from the fresh water media and further to sea by similar estuarine transport. From the view point of estuarine nitrogen processes, the study is mainly concentrated on the influent waters, riverine transports, newer sources acted upon by nitrification as well as bacterial reduction mechanisms, which help to evaluate the fate of three major components namely nitrite, nitrate and ammonia. Identifying the factors affecting the mechanism elucidate information on the outflow by estuarine transport to the sea as well as causing its removal during the cycling processes.

4.2. Inorganic nitrite - nitrogen

Concentration levels of inorganic nitrite-nitrogen both at surface and bottom are given in Table 6. Distribution pattern of nitrite - nitrogen at surface and bottom as time series curve is given in Fig. 8. Annexure 1 [Fig.24(a)] gives the figures of representative seasonal distribution of nitrite - nitrogen. The entire northern parts of the estuary (stns. 1-4) recorded concentration values ranging from 1.07 to 2.56 µg at NO_2^--N l^{-1} at surface and 1.48 to 4.67 µg at NO_2^--N l^{-1} at bottom during monsoon. The monsoonal values gradually increased as the season advanced attaining maximum values during postmonsoon. The postmonsoonal values ranged from 1.68 to 5.58 µg at NO_2^--N l^{-1} at surface and 1.45 to 6.68 µg at NO_2^--N l^{-1} at bottom in this region which gradually decreased to lower values during premonsoon, when the values were limited to 0.77 to 3.58 µg at NO_2^--N l^{-1} at surface and 0.63 to 3.86 µg at NO_2^--N l^{-1} at bottom. A notable feature was the core of high nitrite-nitrogen concentration at the barmouth area (concentration of 5.58 and 6.68 µg at NO_2^- - N l^{-1} at surface and bottom respectively at stn.4) with sharp gradients developing to either sides of the barmouth region during postmonsoon. From the foregoing, it is evident that there is a well defined seasonal variation of nitrite-nitrogen in the northern regions.

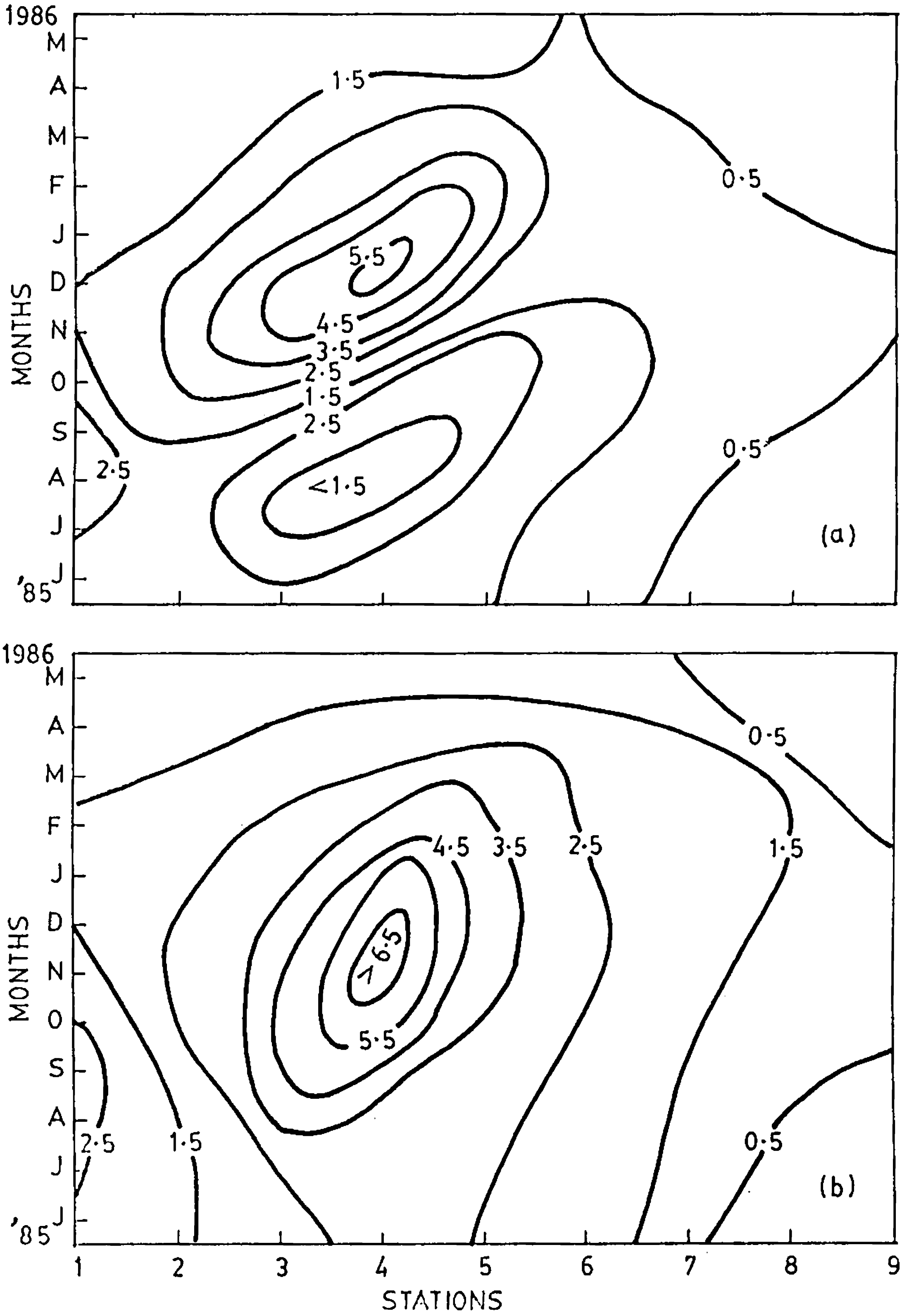

Fig. 8. Time series curve of nitrite - nitrogen (µg at $N\bar{O}_2$-N $\bar{l}^1$) at surface (a) bottom (b).

On the southern parts of the estuary comparatively low concentration of nitrite was observed showing seasonal variation though not as pronounced as on the northern regions. Nitrite - nitrogen in the southern parts of the estuary (stns. 5 - 9) registered values from 0.06 to 2.45 μg at $N\bar{O}_2$-N l^{-1} at surface and 0.23 to 2.47 μg at $N\bar{O}_2$-N l^{-1} at bottom during monsoon. As the season advanced to postmonsoon, slightly higher values were observed with marginal decrease during premonsoon. The minimal seasonal variations in comparison with other parts of the estuary show (i) that the area is a well mixed homogenized water body and (ii) strong influx of freshwater from Muvattupuzha river counterbalancing the tidal currents in the estuary transforming the area to be of riverine nature than estuarine. The premonsoonal values ranged between 0.17 and 2.58 μg at $N\bar{O}_2$-N l^{-1} at surface and 0.30 and 2.61 μg at $N\bar{O}_2$-N l^{-1} at bottom. Bottom values were slightly higher than surface values at all stations throughout the period of investigation due likely to the conversion of nitrite into nitrate-nitrogen in the well oxygenated vertical water column. Like-wise, low surface values observed during July-September around the barmouth region in comparison with higher bottom values, may be suggestive of freshwater outflow across the barmouth, the range of values in the lower layers being mostly controlled by seawater.

The higher values observed in the barmouth region during late postmonsoon (December - January months) may be associated with the increased waste discharged into this region from sewage works and fishing industry. The end of postmonsoon season marks the start of a very active period in the fishery industry in Vypeen area which quantitatively increases the amount of waste discharged into the adjacent estuary. This waste primarily of organic nature, acts as a regenerative external source of nitrogen, contributing to the higher nitrite values observed in this region. A number of earlier workers (Gupta & Pylee, 1964, Nair et al., 1975) have reported high primary production during postmonsoon period coinciding seasonally as well as spatially with the core of high nitrite values presently observed. In this context, it is suggested that the death of organisms after the bloom in late postmosoon and its excreta, may cause the reduction of nitrogenous materials, as partial denitrification of nitrates to nitrites. This mechanism of partial denitrification may account for the variation of nitrites as observed in Fig.8. The variation of ammonia content (see section 4.4) also substantiates the above contention. In addition, the high core of values may be partly due to the effluents discharged from the fertilizer factory on Periyar river bank (7.5 µg at $N\bar{O}_2$-N l^{-1} at stn. Eloor) and from the leachate of adjacent coconut husk retting grounds, with very low DO content.

The earlier study conducted by Joseph (1974) has indicated that nitrite distribution is uniform throughout the year near the barmouth region with higher values in Vypeen channel only (stn. 3 of the present study). This has been attributed to the increasing amount of organic matter in this region, the oxidation of which renders the water column nearly reducing, with the formation of larger amounts of nitrite. The lower values observed during monsoon in the northern regions may be interpreted as due to the excessive dilution caused by low nitrite river waters ($\simeq$ 0.5 µg at $N\bar{O}_2$-N l^{-1}) and direct precipitation. The gradual increase of nutrient values from the southern end of the estuary (stn. 9) to barmouth (stn. 4) indicates very low riverine nitrite inputs into this estuary.

A factor of interest regarding the nitrite distribution in this estuary is the influence of seawater intrusion through Cochin barmouth. In the absence of high riverine nitrite sources, internally generated nitrite and the nutrients from pollutional discharges are distributed in the estuary. The observation of sharp gradients between stns. 3 and 5 during postmonsoon (transition period) indicates the localised effects of seawater intrusion into the estuary. A previous finding by Lakshmanan *et al.* (1987) on the nitrite distribution being modified by the geography of the barmouth region, acting as a barrier between the southern and the northern (the Alwaye branch of Periyar) parts of the estuary is however, not prominently reflected in this study. This is evidenced by the isolines traced across the barmouth from the northern region to the southern parts. The concept of the barmouth region acting as a barrier to cause poor mixing between either parts of the estuary was based on isohaline pattern and not solely on other parametric distribution.

Regressional analysis between nitrite - nitrogen and salinity for three seasons (both surface and bottom) are presented in Fig.9. The highly significant monsoonal correlation observed for this estuary may be associated with the high freshwater discharges containing low amounts of nitrite in the absence of marked salinity intrusion into the estuary. Hence monsoonal nitrite distribution is governed by the riverine discharge.

Two other features observed during the postmonsoon period are (i) the estuary is in a transitional period ie the freshwater - seawater mixing is not rhythmic (ii) enhanced biological activity associated with high primary production occurs during this period.

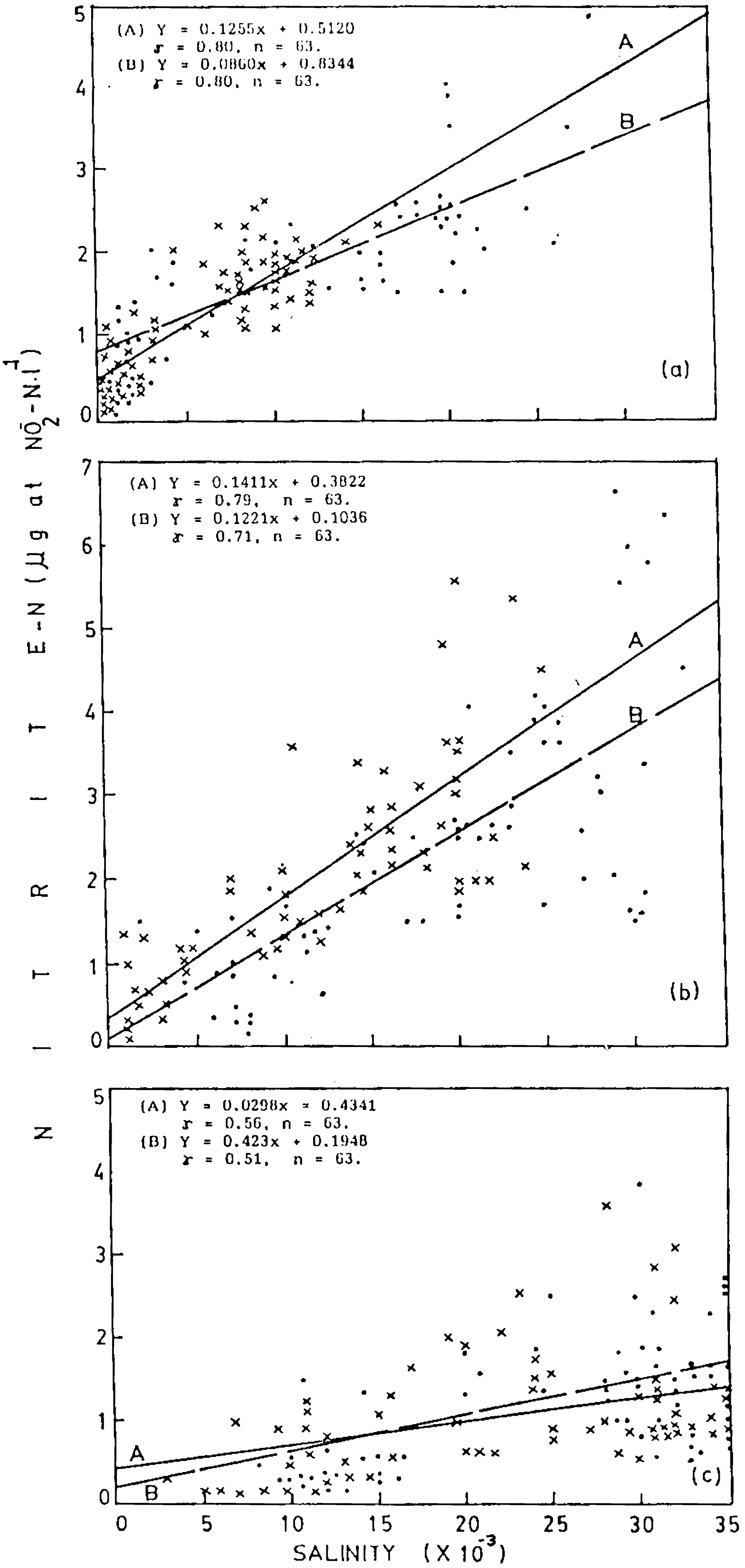

Fig. 9. Relationship between nitrite and salinity

The above two factors have peerless influence on the nitrite distribution giving rise to high scatter of nitrite values against salinity. The main processes controlling the distribution of the nitrite during the period giving rise to significant correlation values may be attributed to the biological processes rather than the hydrodynamical mechanisms. Evidently, the postmonsoonal nitrite distribution in the estuary will have to be viewed as biologically controlled, rather than from the view point of hydrodynamical features.

Nitrite-nitrogen and salinity are also significantly correlated during the premonsoon season; the value of γ being slightly lower than during the other two seasons. The estuarine hydrographical conditions during this period are more defined with respect to seawater intrusion, a situation for which a better correlation could have been expected for this estuary. In the absence of direct influence of seawater the nitrite distribution appears to be at random.

4.3. Inorganic nitrate - nitrogen

Fig.10 indicates the distribution pattern of nitrate - nitrogen in the surface and bottom waters at all stations. Annexure 1 [Fig.24(b)] gives the figures of representative seasonal distribution of nitrate - nitrogen. The nitrate concentration (Table 7) in surface waters of the northern region (stns. 1-4) varied widely: 8.76 to 30.95, 9.30 to 20.15 and 3.10 to 14.18 µg at NO_3^--N l^{-1} during monsoon, postmonsoon and premonsoon seasons respectively. The bottom waters recorded slightly higher values than those of surface, which varied from 13.46 to 38.95, 10.66 to 26.48, 4.68 to 14.70 µg at NO_3^--N l^{-1} during monsoon, postmonsoon and premonsoon respectively. The formation of high core during monsoon at barmouth (stn.4) is a notable feature.

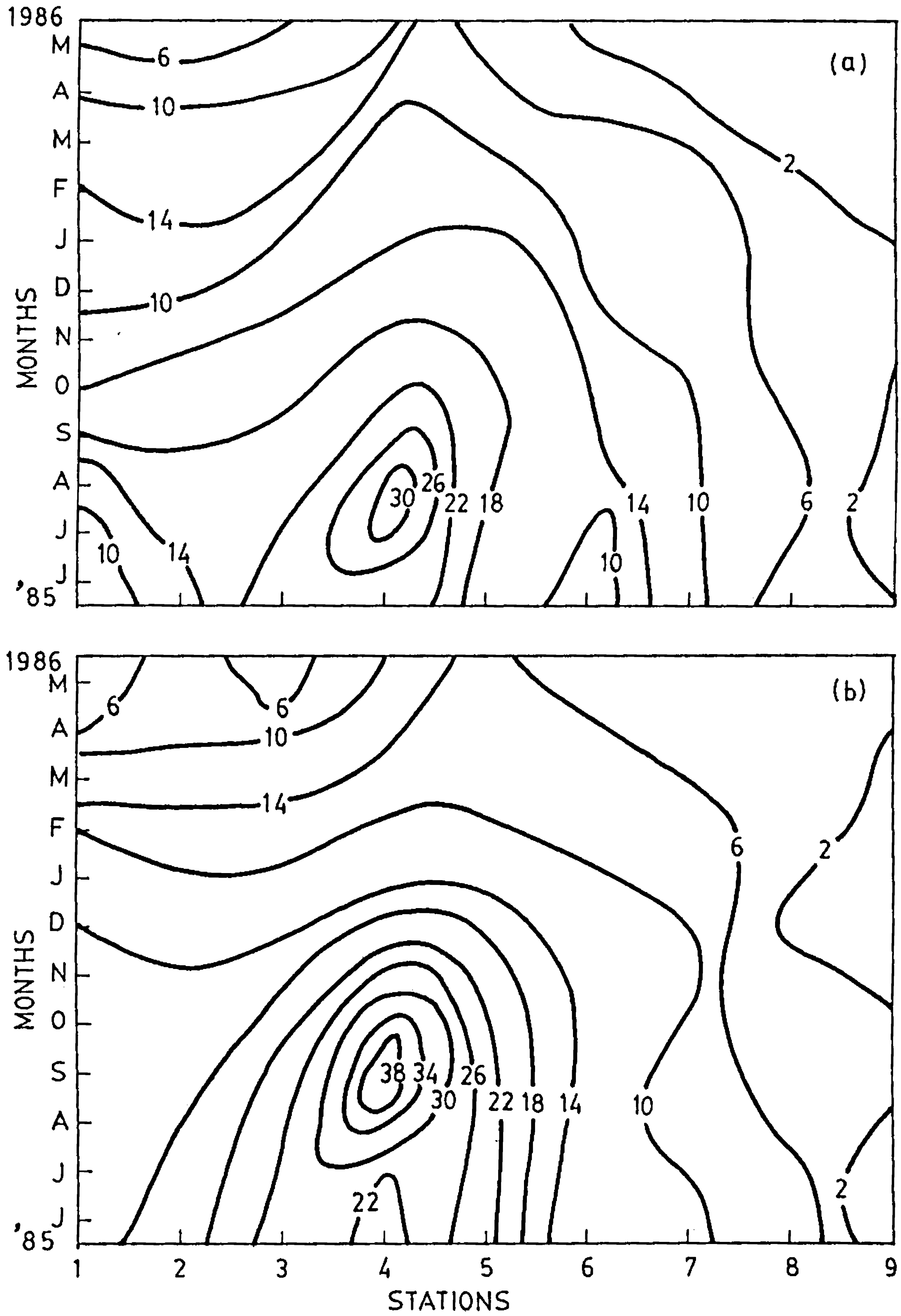

Fig. 10. Time series curve of nitrate - nitrogen (µg at $N\bar{O}_3$-N l^{-1}) at surface (a) and bottom (b).

The distribution pattern on the southern parts indicates the gradual decrease of concentration of nitrate from the barmouth region to the southern tip of the estuary for all seasons during the period of investigation. The surface values varied from 0.74 to 19.70, 0.86 to 18.32 and 0.16 to 13.60 µg at $N\bar{O}_3$-N l^{-1} during monsoon, postmonsoon and premonsoon respectively. Bottom values ranged from 0.80 to 25.41, 0.98 to 22.31 and 0.80 to 10.61 µg at $N\bar{O}_3$-N l^{-1} during monsoon, postmonsoon and premonsoon respectively with no singled out feature as observed on the northern parts.

The study indicates the presence of cores of high values during monsoon on the northern as well as on the southern parts of the barmouth region. This is in agreement with the observation of Manikoth & Salih (1974) reporting high values of nitrate during monsoon on the northern parts of the Cochin barmouth. The observed range of value for nitrate is comparable with those observed by earlier workers (Sarala Devi et al., 1983). These findings of higher nitrates during June-August months reflect the general trend of nitrate leaching from land drainage reaching the coastal waters.

The high values of nitrate around the barmouth area are however, confined between stns. 4 and 5 on the southern parts and to stn. 2 on the northern parts. This feature is more prominent along the bottom layers of the estuary giving rise to vertical gradients in the region of the above stations. A possible mechanism giving rise to this phenomenon may be the influx of forestshed leached nitrate in freshwaters flowing through Periyar river which also contain oxidisable organic detritus matter. Auxiliary studies held during monsoon period in conjunction with the present investigation in the lower

Periyar reaches have revealed the movement of bed load sediment of high organic content, derived from coconut husk retting grounds. The retting grounds, by themselves are high nitrite and nitrate production zones as reported by Remani et al. (1981). The organic rich sediments transported to the barmouth region is retained in this region and is oxidised with the liberation of nitrates to the overlying waters, which is mostly saline. The abundant availability of nutrient nitrates to this region, subsequently paves way for high primary production during the postmonsoon season. This is as well indicated by the decrease of nitrate values between stns. 2 and 5 associated with partial denitrification cited earlier.

The premonsoonal low values observed earlier by Sankaranarayanan & Qasim (1969) and Manikoth & Salih (1974) are also observed during the present study. There is minimal freshwater inflow contribution to the estuarine nitrates; from the only other source, namely seawater, it is also, however, low. The steady decrease of nitrate values from stns.4 to 9 confirms the above view. The ability of seawater to leach nitrogenous compounds from the sediments is also excluded in the absence of organic detritus matter. Hence the nitrate nitrogen distribution in this estuary may be seasonally demarcated as: (i) the monsoon period by high nitrate bearing land drainage run off, flowing into the estuary as river discharge; seawater releasing nitrates for recycling within the estuary, by acting upon the organic rich sedimented materials transferred to the lower estuary; monsoonal precipitation adding $N\bar{O}_3$-N to the already high values of estuarine nitrates (ii) postmonsoon period of higher biological activity (primary production) regulating the concentration and distribution of nitrates in the estuary (iii) premonsoonal period of low flux from either riverine or oceanic sources limiting nitrate concentration to low values; possibility of nitrogenous matter being evolved from sediments is insignificant to influence the nitrate concentration of overlying water.

Regressional analysis (Fig. 11) to elucidate information on the correlative behaviour between nitrate and seawater brings out the following features. Mechanisms working in this estuary appears to support the view of conservative mixing during most periods of the year. Generally, the removal processes, if any, will have to occur with increasing salinity towards the seaward side. The monsoonal values are observed to be higher, occurring in the moderate saline waters when low values were observed in the freshwater region. The linkage of high nitrate during monsoon in the salinity range, 10 to 20 x 10^{-3}, corresponds to an area where leaching of organic matter takes place. The relative roles of seawater influenced hydrodynamical distribution and biologically controlled nutrient values of nitrate being dissimilar and non-categorised, the postmonsoonal lower values are scattered in the entire salinity scale of 0 to 35 x 10^{-3}.

During the premonsoon season also, the two parameters are correlated with higher values occurring more frequently in the high salinity region. Lakshmanan *et al.* (1987) have also made similar observation. Similar analysis conducted in Tamar river estuary by Morris *et al.* (1981) and Knox *et al.* (1986) have also found no evidence of nitrate removal for the sub-tropical waterways. This study also confirms the above contention, suggestive of similar operative mechanisms on distribution and regeneration of nitrate-nitrogen in both tropical as well as subtropical estuaries.

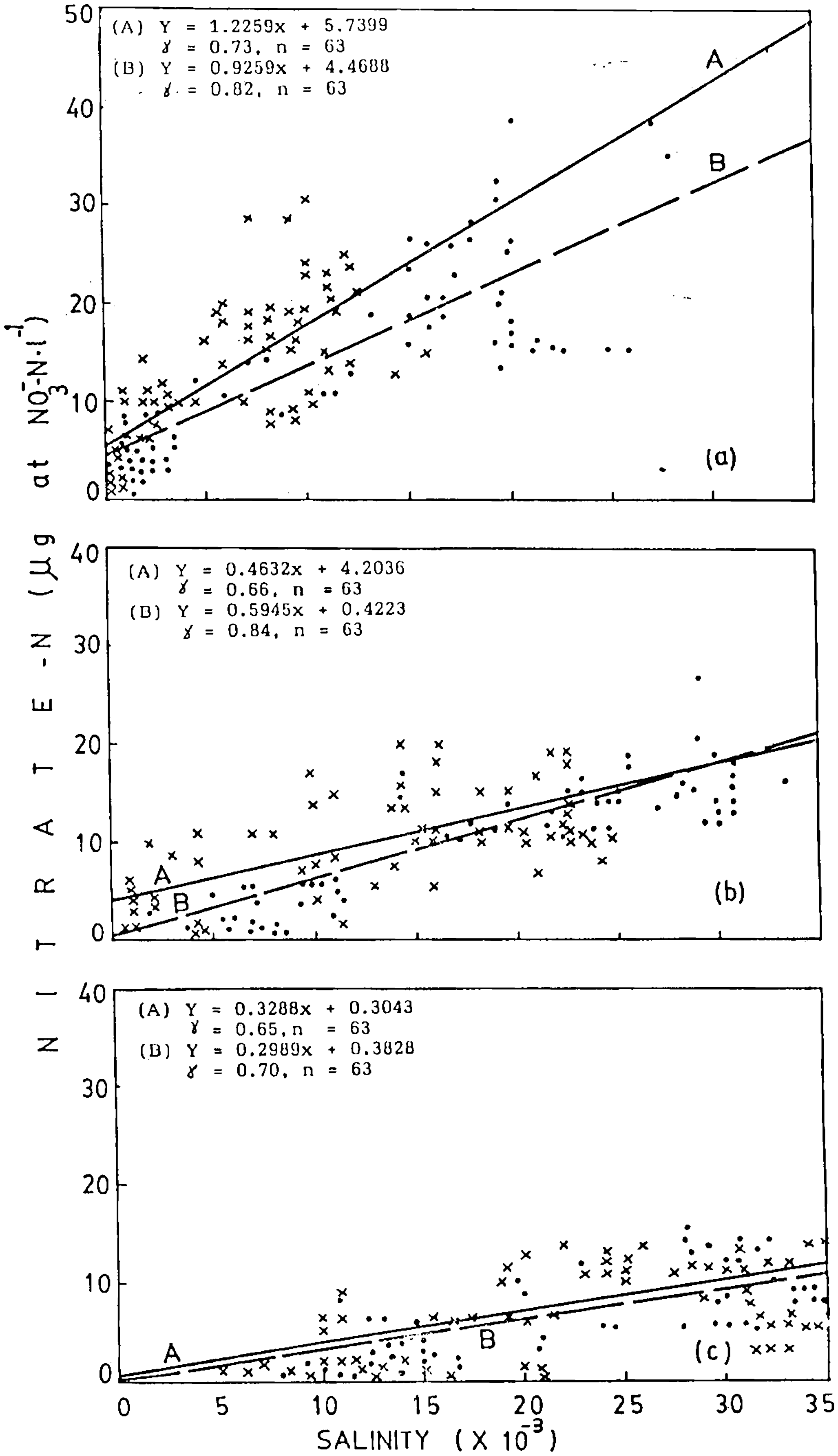

Fig. 11. Relationship between nitrate and salinity during

4.4. Ammonia-nitrogen

Concentration levels of ammonia - nitrogen both at surface and bottom are given in Table 8. Annexure 1 [Fig.24(c)] gives the representative figures of seasonal distribution of ammonia - nitrogen. Fig. 12 represents the seasonal distribution of ammonia - nitrogen. Ammonia content in the estuary ranged from negligible values on the southern parts to 24.46 µg at NH_3-N l^{-1} on the northern parts. The maximum value was recorded during monsoon at stn. 3 and values ranged from 0.05 to 21.10 µg at NH_3-N l^{-1} at surface and 0.05 to 24.46 µg at NH_3-N l^{-1} at bottom, which steadily decreased to a minimum as the season progressed to postmonsoon. The minimum values ranged from 0.05 to 11.00 µg at NH_3-N l^{-1} at surface and 0.05 to 12.54 µg at NH_3-N l^{-1} at bottom during postmonsoonal and early premonsoon.

The isoline pattern of ammonia-nitrogen distribution in the estuary indicates four major features: (i) a well marked high concentration region on the northern part adjacent to the barmouth during monsoon period (ii) postmonsoonal decrease of concentration in the zone of high production (stns. 2 to 4) (iii) marginal increase during premonsoon in the bottom layers (stns. 2 to 4) whereas the trend indicates lowering in the surface waters (iv) irrespective of seasonality, the southern parts of the estuary contain little or negligible amounts of ammonia except in the vicinity of the Cochin harbour (stn. 5; 6.0 µg at NH_3-N l^{-1}).

The above features show some similarity to the nitrate distribution in this estuary, specifically the formation of high concentration regions on northern parts identical in time as well as in location.

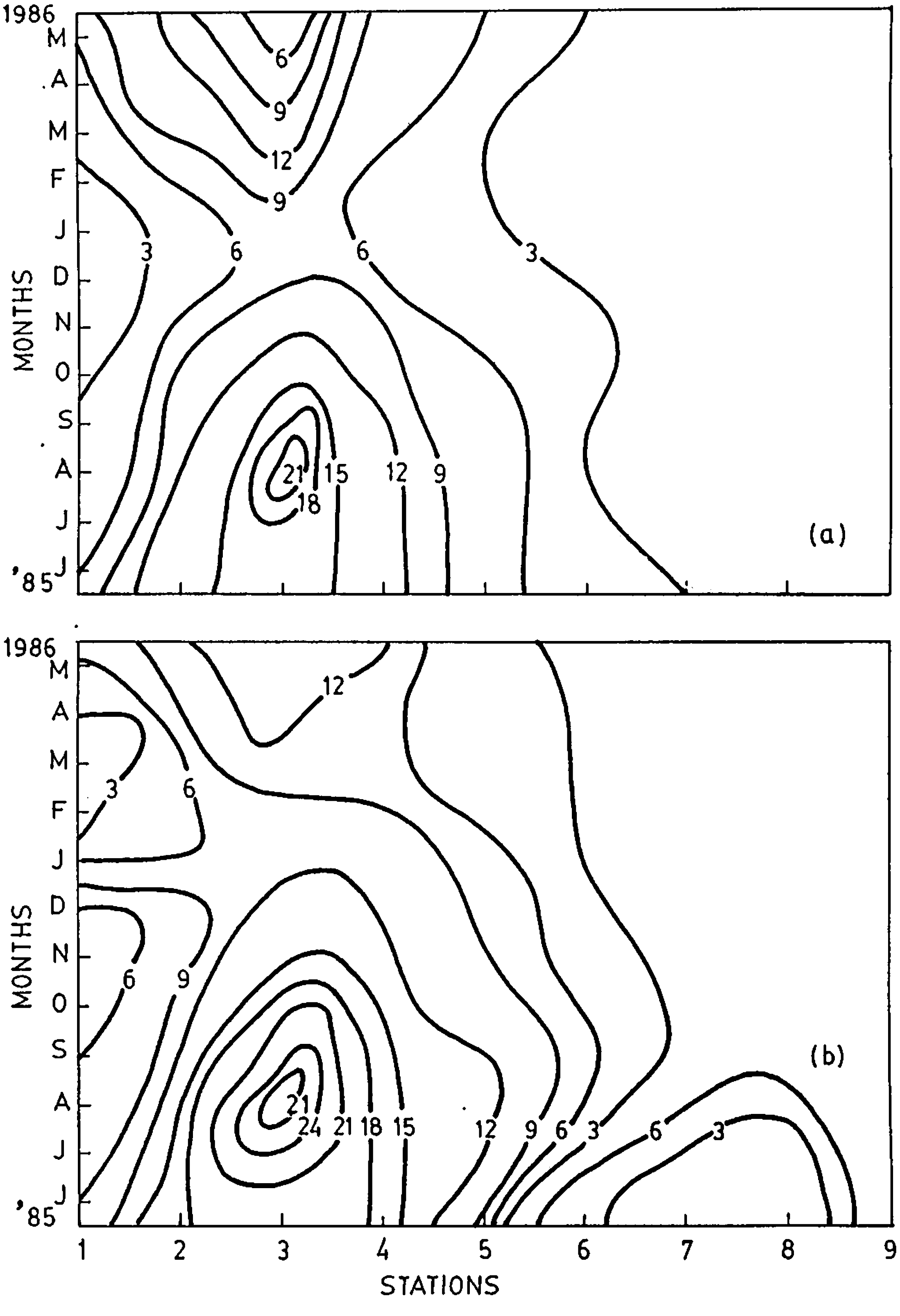

Fig. 12. Time series curve of ammonia - nitrogen (µg at NH_3-N l^{-1}) at surface (a) and bottom (b).

It is assumed that this feature is closely interlinked to the formation of nitrates via the ammonia-nitrite chain. The monsoon season exhibits the transfer of nitrogenous materials associated with previously sedimented matter to the deeper parts of the lower estuary; and subsequently under oxidising condition, the organic matter is decomposed by nitrifying bacteria, first to ammonia and to the intermediatory nitrites (sparingly observed as $N\bar{O}_2$-N) to the final oxidation state of nitrate-nitrogen. The conversion of ammonia evolved on the decomposition of organic matter is also influenced by the presence of seawater converting the same to nitrate in a rapidly occurring reaction in this environment. Addition of ammonia brought to the estuary during the monsoon rainfall though not quantified, is however, not excluded.

Yet another feature associated with the biological aspects of the estuary is the rapid utilization of nitrogenous compounds during postmonsoon periods. As in the case of nitrates, ammonia is also being consumed during photosynthetic activity in the northern part of the estuary. This results in the progressive depletion of ammonia during the postmonsoon period (stns. 2 to 5). In comparison with bottom layers the amount of ammonia content in the surface waters are considerably low. It may also be noted that part of the ammonia present in the media results in its conversion to nitrite observed from Fig.8. It is felt that evolution of ammonia continues during premonsoon period also especially in the northern parts of the estuary. This is evidenced by the increase of ammonia values along the bottom layers of the northern part of the estuary. Nair et al. (1975) have reported bimodal periods of enhanced biological activity by way of primary production, occurring during postmonsoon and premonsoon in this region. This factor has also been noticed by earlier workers (Gupta & Pylee, 1964). The lowering of surficial ammonia content may be associated with the above reason at stns. 2 to 4.

The southern parts of the estuary, more or less in a homogenized condition (vertically well mixed) causes the even distribution of ammonia-nitrogen irrespective of seasons. The contribution from river discharges and regeneration from sedimented materials (mostly sandy) is negatived. In this background, the southern part of the Cochin estuary only retains negligible amounts of ammonia as compared to the northern parts. Marginal ammonia values in the area between stns. 4 to 6 in the bottom layers is associated with the extension of seawater intrusion along the Mattancherry and Ernakulam channels, translating the effect of peak values observed at stn. 3.

CHAPTER 5

PHOSPHORUS IN THE ESTUARY

The behaviour of phosphorus in aquatic ecosystems, both in freshwater and marine environments, has been the subject of many scientific studies. Phosphorus predominantly occurs in nature as orthophosphate, with oxidation number V and coordination number 4 and is of great importance to a wide variety of biological and chemical processes.

In conjunction with nitrogen, the presence of phosphorus in a system satisfies the major needs for nutrients. Phytoplanktons normally satisfy their requirements of this element by the direct assimilation of orthophosphate (Riley & Chester, 1971,b). The mechanism of cycling of phosphorus as a nutrient to the growth of phytoplankton and zooplankton depends on a complex set of biologically mediated reactions. The inorganic phosphate is converted primarily in the biota to form adenosine triphosphate (ATP) and adenosine diphosphate (ADP) which are generally considered to supply, by their reactions, the energy requirements for all biochemical reactions of the organism. Soluble phosphorus is taken up by phytoplankton along with nitrate in relatively constant proportions and these elements are released upon decomposition of the phytoplankton. Although variations in the N-P ratio do occur, these stoichiometric relations are most readily explained in terms of the simplified equation given below:

$$106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122\ H_2O + 18\ H^+\ (+\ \text{trace elements, energy})\ \underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftharpoons}}\ \underset{\text{algal tissue}}{(C_{106}\ H_{263}\ O_{110}\ N_{16}\ P_1)} + 138\ O_2 \qquad (5.1)$$

Phosphates are used in industrial water softening processes where their ability to form sparingly soluble calcium salt is utilized. Also condensed inorganic phosphates are employed as agents for complexing Ca^{2+} and Fe^{3+} in boiler waters, as "threshold treatment agent" and as builders in synthetic detergent formulation because of a synergistic reaction with the surfactants necessary for detergent action.

Phosphorus* may be present in water bodies in various inorganic and organic forms: dissolved, particulate or colloidal. Dissolved inorganic phosphate composed of ions such as PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ and their concentration and distribution in the hydrosphere are governed by pH:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad (5.2.)$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad (5.3)$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad (5.4)$$

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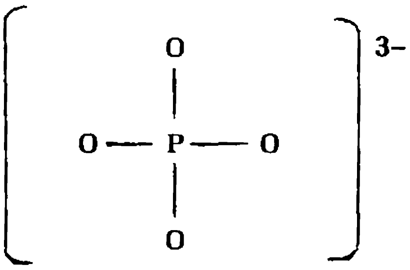
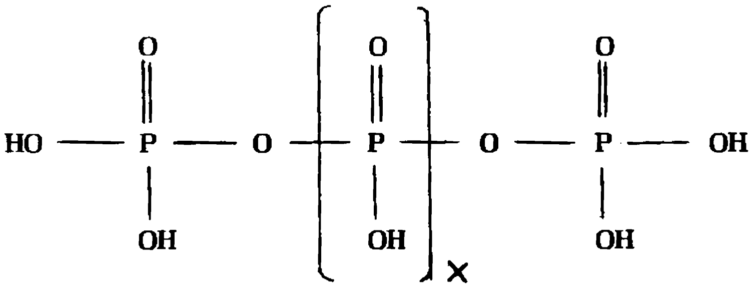
* The term phosphate and phosphorus are often used synonymously in aquatic sciences.

At the normal pH range of 5 to 9 the predominant dissolved inorganic phosphate species is HPO_4^{2-} (about 90%) with some $H_2PO_4^-$. Information on the pH dependent distribution of these species is required in interpreting the solubility behaviour, complex formation, and sorption processes of phosphorus in water (Stumm & Morgan, 1970). Of the above three dissolved forms, commonly estimated species is the orthophosphate as PO_4^{3-} ions. Phosphate occurs in minerals as orthophosphate anion in which P atom is centrally bonded to the oxygen atoms, which are located at the four corners of a tetrahedron as:



$$\left[\begin{array}{ccc} & O & \\ & | & \\ O - & P & - O \\ & | & \\ & O & \end{array}\right]^{3-}$$

Abundance of the condensed phosphates such as polyphosphate and metaphosphate, though not yet detected in seawater, is thought to be present in coastal and estuarine waters as a result of pollution from detergents (Koroleff, 1983,b). The concentration of condensed phosphate in surface waters are highly variable because they are subjected to continued hydrolytic breakdown to orthophosphate. (Stumm & Morgan, 1970). The polyphosphates have the structure



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\left[\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}\right]_X-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$$

The sodium tripolyphosphate (X = 1) is generally used in detergents (Mullins, 1977). These are converted to the uncondensed phosphate in solution by hydrolysis catalysed by acids:

$$P_3O_{10}^{5-} + 2H_2O \longrightarrow 3\ HPO_4^{2-} + H^+ \qquad (5.5)$$

Phosphorus in natural waters occur mostly in the organic form usually associated with complex cellular substance (Wetzel, 1975). Waste water effluents and agricultural soil drainages contain considerable amount of organically bound phosphate. It is estimated that 30-60% of the total phosphorus present in natural waters is organic phosphorus, of which 70% or more occurs as particulate organic phosphates, the balance being in dissolved or colloidal state (Snoeyink & Jenkins, 1980). Though the nature of these organic compounds are uncertain, nucleic acid material, phospholipids and many decomposition products are detectable (Solorzano & Strickland, 1968).

Kuenzler (1970) has shown that certain marine algae satisfy their phosphate requirement by direct assimilation of dissolved organic phosphorus, when the inorganic phosphorus level becomes low enough to limit algal growth. However, the utilization of dissolved organic phosphorus is proportional to the activity of phosphate esters which are present in their cells. The release of orthophosphate occurs from dissolved organic phosphorus by the activity of alkaline phosphate, which is found to be negatively correlated with orthophosphate concentration in seawater (Hashimoto et al., 1985). The activity of phosphate esters depend on various physical, chemical and biological factors which are important for understanding the role of these esters in phosphorus cycling (Siuda, 1984).

Particulate phosphorus exists in two forms: inorganic as well as combined organic derived from organic detritus materials. Watt & Hayes (1963) have suggested that a net influx of particulate phosphorus occurs associated with an increase of particulate matter in the area. Processes involving inorganic particulate phosphorus, however, may have significant effect in controlling the concentration of dissolved orthophosphate ions. The conversion of particulate phosphorus to dissolved phosphorus occurs as a result of the bacterial attack, followed by uptake by phytoplankton with subsequent transformation to dissolved forms.

The biogeochemical cycle of phosphorus in the estuarine environment and its distribution and seasonal variations have been reported by many authors (Correll et al., 1975; Aston, 1980). Phosphorus cycling through the biological system is generally similar to nitrogen cycling, though less complex. Biogeochemistry of phosphorus in estuaries is controlled by a combination of physical, chemical and biological processes. These processes generally fall into three categories: (i) addition of phosphorus to the active pool by various processes like input, decomposition of particulate matter and regeneration (ii) removal of phosphorus from the active pool by precipitation or physical removal and (iii) uptake or concentration of phosphorus by living organism, consumers or destroyers (Martin,1970).

Rivers are the major source of phosphorus input to the estuarine environment. In estuaries, the riverine influx of phosphorus may be substantially modified by deposition or dissolution changing the quantity of phosphorus (Fox et al., 1985). The weathering of relatively insoluble ferric or calcium phosphate rocks and land drainage also delivers phosphorus to estuaries as phosphate minerals in suspended form (Martin, 1970). Other external sources of phosphorus contributed to estuaries may be from domestic sewage, and effluents from fertilizer units. It is well known that sediments can act as a reservoir for phosphorus, capable of supporting aquatic growth for an infinite period of time without any input of additional nutrients from any external source (Frink, 1967). The exchange of phosphorus between sediment and overlying waters is a major component of the phosphorus cycle in the estuarine environment. Mountainous region of crystalline geomorphology generally record lowest phosphorus values, however, slightly higher values were observed in low land waters derived from sedimentary rock deposits (Wetzel, 1975).

Typical concentrations of phosphorus found in various water systems in various forms are given in Table 9; the concentration of phosphorus in some of the estuaries - viz. Tamar (UK), Delaware (USA), and Mandovi-Zuari (India) are also given in the same Table.

The concentration of total phosphorus in unpolluted surface waters ranges between 0.3 and 1.3 µg at l^{-1} (Stumm & Morgan, 1970) but levels as high as 65.0 µg at l^{-1} are not uncommon in lake waters receiving heavy domestic and agricultural drainage. Sarala Devi et al. (1983) have presented data on the phosphate content of some estuaries situated along north Kerala Coast. In general, the levels encountered in these estuaries ranged from 0.00 to 10.41 µg at l^{-1} with higher amounts present during monsoon.

A significant depletion in the content of phosphorus occurs in the surface waters corresponding to an increase of phytoplankton population density. Phosphorus concentration and phytoplankton density follows an inverse relation to one another. This relationship indicates that the concentration of phosphorus in surface waters is in a dynamic state and variations are mainly brought about by biological production. Abundant phosphate availability from discharge of raw or treated waste water or from intensive use of fertilizers or from urban run off enriched by detergents stimulates undesirable plankton bloom; this phenomenon is generally known as "eutrophication" (Rand et al., 1976). Subsequent decay of plants and organisms cause oxygen depletion; organic compounds present in the tissues are rapidly converted to the dissolved forms, which on bacterial oxidation release the phosphate in the ionic forms.

Sholkovitz (1976) and Butler & Tibbitts (1972) have shown that non-biological reactions may also contribute to the control of estuarine phosphorus distribution. From the combined field and laboratory experiments conducted by Patrick & Khalid (1974), it was suggested that the phosphate concentration in the estuarine environment is significantly affected by mineral-water reactions. The formation of complex chelates and insoluble salts between major cation and various phosphate anions may have profound effect on the phosphate distribution (Stumm & Morgan, 1970).

Recently several studies have been made on phosphorus controlled/influenced biological cycles in individual estuaries. The first detailed study on inorganic phosphate in estuaries was conducted by Stefansson & Richards (1963) who noted that there was a distinct lack of variation of dissolved phosphate concentration in estuarine waters which could be attributed to: (i) the similarity of inorganic phosphate in the river water and seawater which contribute to the estuary and (ii) the effect of buffering mechanism. Correll et al. (1975) have investigated the phosphorus flux and cycling in the Rhode river estuary and concluded that phosphate is taken up from solution in brackish waters by bacteria, mainly located on the surface of organic detritus and suspended mineral and by phytoplankton under the appropriate light intensity condition. The non-conservative behaviour observed by Peterson et al. (1975,a) & Hobbie et al. (1975) in some estuaries are attributable to biological degradation processes. The behaviour of phosphorus in the Tamar estuary was studied by Morris et al. (1981); non-conservative behaviour observed in the low salinity region is interpreted as due to the non-biological removal of phosphate through precipitation of iron. Recent studies by DeSousa (1983) on the behaviour of nutrients in the Mandovi estuary showed very low concentration of phosphorus; variability in low salinity range attributed to the buffering effect of estuarine waters.

In polluted waters the sediments, especially from reclaimed land, removes a large proportion of dissolved phosphate so that the chances of eutrophication would be reduced (Stirling & Wormald, 1977). Laboratory and field observation showed that adsorption is reversible and sediments act as a phosphate buffer for keeping the phosphate concentration in the overlying waters constant (Pomeroy et al., 1965 & Harter, 1968). Hence phosphate buffering mechanism is of considerable importance in controlling the fertility of the overlying waters.

Golterman (1973) suggested that when phosphorus is adsorbed onto sediment minerals, one fraction is adsorbed into anionic sites and another into the crystalline lattice structure by substitution of hydroxyl ion. The principal factors controlling the exchange processes are redox potential (Mortimer, 1971), pH (Burns & Salomon, 1969) and concentration of calcium and magnesium of overlying water (Upchurch et al., 1974). A large proportion of phosphorus is adsorbed onto ferric hydroxide which on redissolution releases phosphorus. This condition occurs when the dissolved oxygen is less than 2 mg l^{-1} (Kramer et al., 1972). The rate of phosphorus release from the sediment increases markedly with increasing turbulence and in fact doubles, if the sediments are resuspended (Zicker et al., 1956); phosphate exchange capacity between sediment and overlying water appear to be related to the texture of the sediment also (Venkataswamy Reddy & Hariharan, 1986).

Phosphate distribution in Cochin estuary shows a marked seasonal variation influenced by local precipitation and land run off. Sakaranarayanan & Qasim, (1969) observed very high phosphate values during monsoon and vertical homogenity with very low phosphate content during premonsoon period in Cochin estuary. Shynamma & Balakrishnan (1973) did not observe any definite pattern of variation in inorganic phosphate concentration and any correlation with other parameters. However, Joseph (1974) reported high values of phosphate during premonsoon which exceed the limit of water pollution standards and low values during monsoon period associated with high values of silica content. Lakshmanan et al. (1987) have discussed the seasonal distribution and variation of phosphorus in Cochin backwaters, extent of influence from industrial effluent discharges and urban sewage and the behaviour of phosphorus resulting from interbasin transfer of water and construction of Thanneermukkum bund.

The distribution of mud phosphates in the Cochin estuary was studied by Ansari & Rajagopal (1974); they observed that amount of adsorbed phosphate was generally higher than interstitial phosphate and that fine sediment of silt and clay was associated with higher content of phosphate than the coarse sandy sediment. The total phosphate concentration revealed a decreasing trend from marine to the estuarine zone. Since the Cochin estuary is shallow, it was thought that one of the major factors governing the distribution and variation of phosphorus may be the difference in the regenerative property of the bottom sediment (Reddy & Sankaranarayanan, 1972). Their experiments on the phosphate regenerative activity of the muds of Cochin estuary revealed that sediments from high saline brackish water released phosphate continuously to overlying waters whereas the mud from less saline brackish area adsorbed phosphate from overlying water.

Perusal of the literature shows that the studies in Cochin estuary is chiefly concerned with the distribution of orthophosphate. Having recognized the presence of various types of phosphorus in estuarine waters the present study provides a detailed account of various types of phosphorus, their distribution and their relevance with regard to mud phosphorus (interstitial and adsorbed).

5.1. Inorganic reactive phosphorus

Concentrations of inorganic reactive phosphorus at stns. 1-9 during June 1985 - May 1986 are given in Table 10. Time series curves of inorganic reactive phosphorus (IRP) both at surface and bottom are recorded in the Fig. 13. Annexure 2 [Fig. 25(a)] gives the figures of seasonal distribution of IRP. On the northern region the values ranged from 0.27 to 11.61 µg at PO_4^{3-}-P l^{-1} at surface and 1.032 to 15.61 µg at PO_4^{3-}-p l^{-1} at bottom. Low monsoonal values ranging from 0.28 to 4.90 µg at PO_4^{3-}-P l^{-1} at surface and 1.03 to 5.10 µg at PO_4^{3-}-P l^{-1} at bottom were observed; these values gradually increased during postmonsoon and premonsoon. The premonsoonal values ranged from 0.27 to 11.61 µg at PO_4^{3-}-P l^{-1} surface and 2.48 to 15.61 µg at PO_4^{3-}-P l^{-1} at bottom.

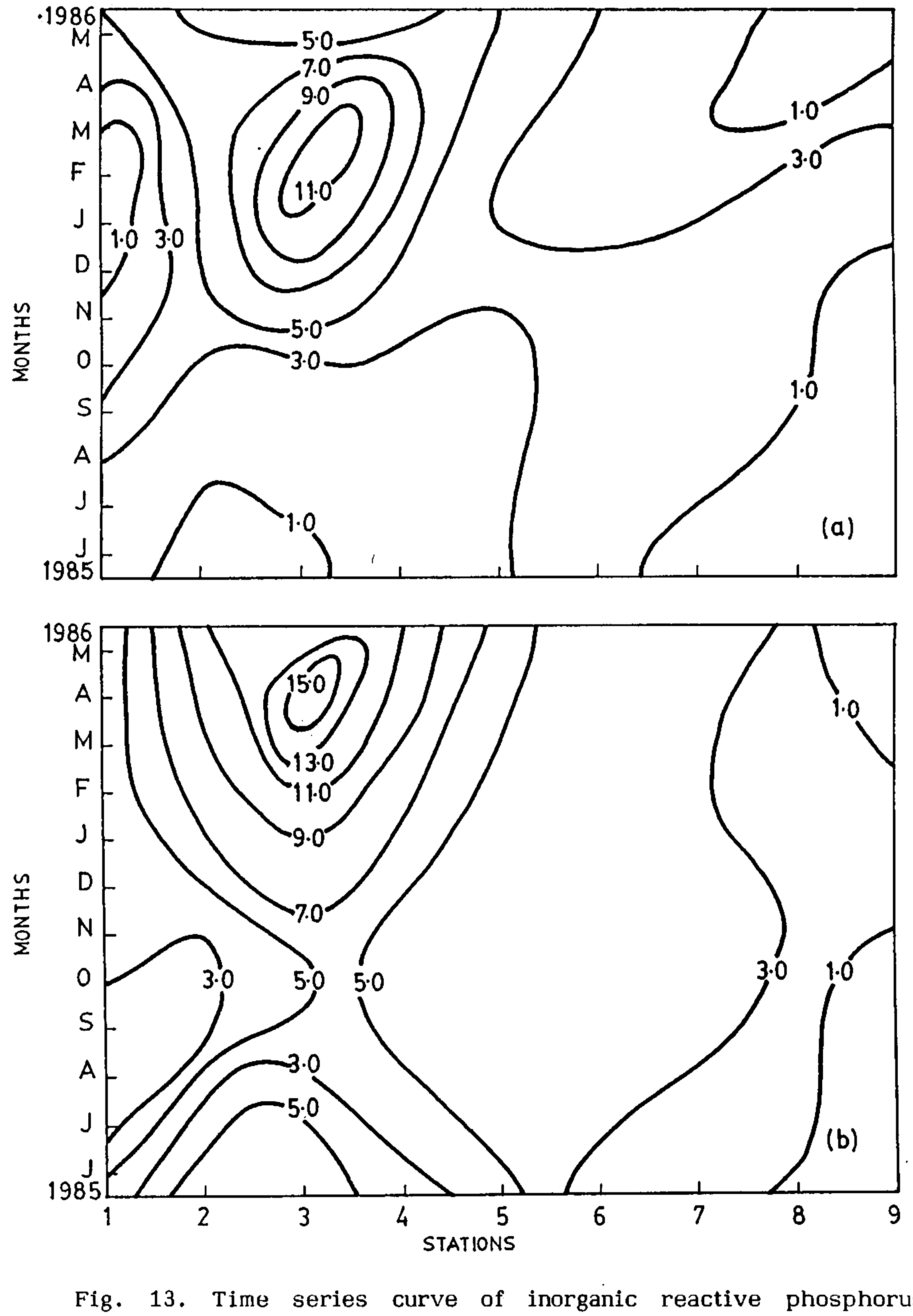


Fig. 13. Time series curve of inorganic reactive phosphorus (µg at PO_4^{3-}-P l^{-1}) at surface (a) and bottom (b).

Domestic sewage, effluents from the fertilizer complex and loading/unloading of fertilizers/rockphosphate at Cochin harbour channel are known external sources of phosphorus in this estuary. Internal source of phosphorus might be its regeneration from the bottom sediments under favourable condition. The present investigation showed a seasonal variation generally exhibiting lower values during monsoon to very high values in premonsoon. The low values observed during monsoon indicates dilution of estuarine water by freshwater of low phosphate content. The low values may also be due to the removal by adsorption caused by the influx of silt-laden freshwater. Increased riverine discharge during this period results in low salinity and lowering of pH along with highly oxygenated conditions favouring the removal of phosphorus from the overlying waters by sedimenting particles. Several workers (Pomeroy et al., 1965; Liss, 1976; Nagarajaiah & Gupta, 1983) have also reported that the removal of phosphate from the overlying water by suspended sediments is associated with low salinity, low pH and highly oxygenated conditions.

The present work shows a gradual increase of IRP associated with increasing salinity and decreasing DO. An important feature is that during premonsoon, wide variation in phosphorus content occurred from station to station giving rise to horizontal gradients both at surface and bottom layers. The high values observed during premonsoon, particularly at stn. 3 is associated with low values of fresh water fraction (0.20 - 0.28). This clearly suggests that in addition to the transport of industrial effluents in the freshwaters from Periyar river and from nearby land drainage, some other factors play a critical role in the enrichment of phosphorus content in the northern region. Domestic sewage, loading and unloading of rock phosphate and fertilizers at Cochin harbour may contribute to the formation of a high core of phosphate content in this region. Reddy & Sankaranarayanan (1972) have attributed the large seasonal variation of phosphate content in the Cochin backwaters to the regeneration of phosphorus from sediment. The increase of salinity with decrease of DO during premonsoon in the northern region favours the desorption of phosphorus from the sediments; the high values of IRP observed during premonsoon may be also partly due to the release of phosphorus from the sediments. The earlier studies also reported high concentration of dissolved phosphate in this region, during premonsoon (Joseph, 1974; Lakshmanan et al., 1987).

In the southern region IRP concentration ranged from 0.00 to 3.47 µg at PO_4^{3-}-P l^{-1} at surface and 0.00 to 4.63 µg at PO_4^{3-}-P l^{-1} at bottom during monsoon. Slightly higher amounts of phosphorus are recorded during postmonsoon and premonsoon; premonsoonal values ranged from 0.41 to 3.74 µg at PO_4^{3-}-P l^{-1} at surface and 0.00 to 5.87 µg at PO_4^{3-}-P l^{-1} at bottom. A significant observation made from the distribution of inorganic reactive phosphorus was the lower values recorded in the southern region (stns. 4-9) both at surface and bottom during monsoon and postmonsoon. The values of phosphorus gradually increased from southern tip to the Cochin barmouth. All these features indicate the low inputs of phosphorus from river discharge and land drainage. Higher turbidity observed during monsoon may also facilitate the adsorption in the shallow southern parts of the estuary.

The variation of inorganic reactive phosphorus with salinity is shown in Fig. 14 along with regressional lines. The results indicate that there is a distinct lack of variations of phosphorus in the estuary especially in lower salinity zones. Phosphate showed very low concen-

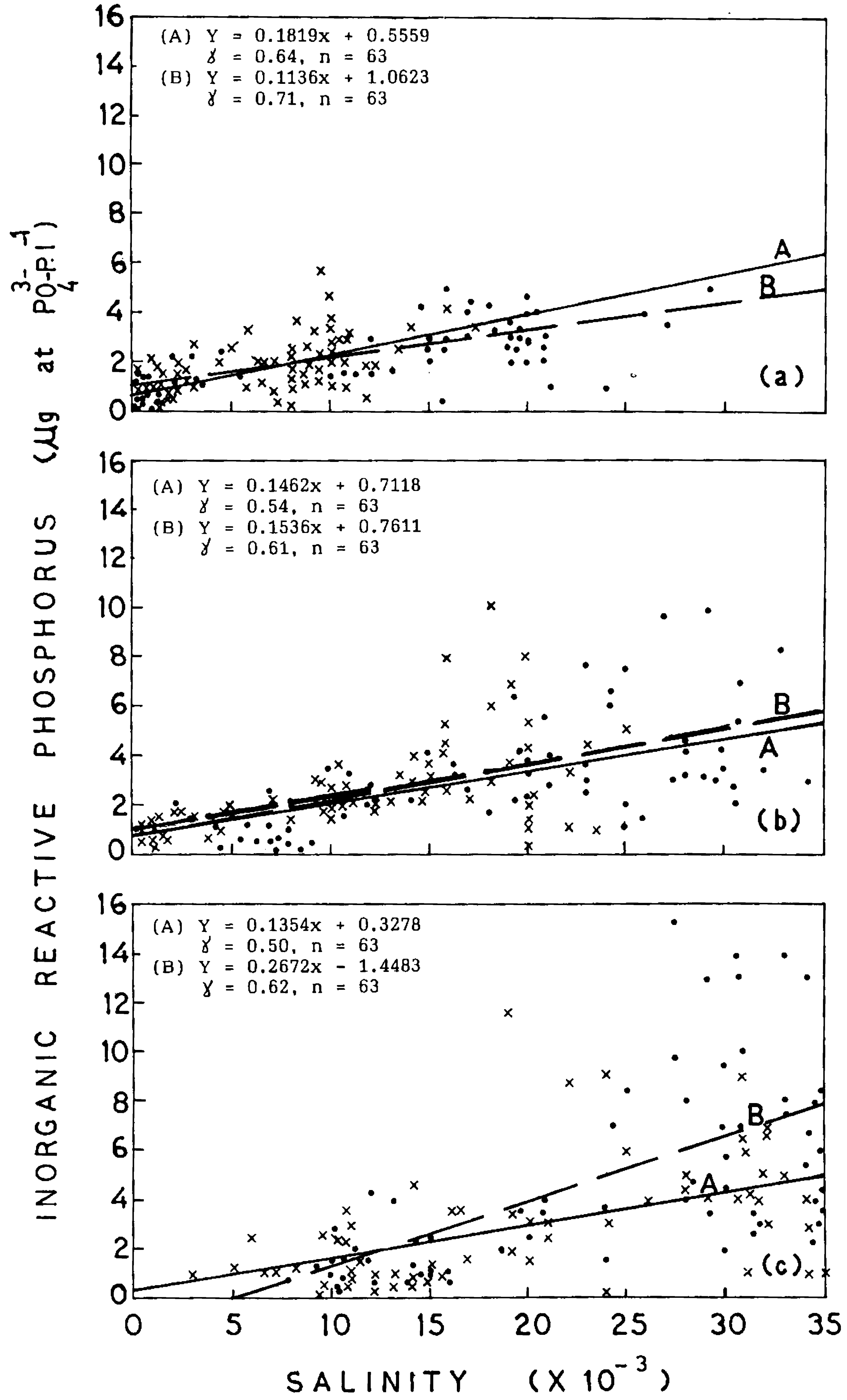


Fig. 14. Relationship between inorganic reactive phosphorus and salinity during monsoon (a), postmonsoon (b) and

tration in low salinity region, however, its concentration increased slightly towards the high salinity region. Stirling & Wormald (1977) observed that upto 99% adsorption of phosphate occurs at a salinity of $\simeq 2 \times 10^{-3}$. When the seawater with pH of about 8 mixes with river water of lower pH in estuaries, the efficiency of phosphate removal will be greater in the low saline regions than in the higher salinity waters of the estuary. This accounts for the lower concentration of dissolved phosphate towards the southern tip of the estuary. A similar feature was observed by DeSousa (1983) in Mandovi-Zuari estuarine system. In addition to the above factors, biological utilization will also contribute to the variation of phosphate concentration. The earlier studies on primary production conducted by Gupta & Pylee (1964) and Nair et al. (1975) reported very low productivity in the southern region of the estuary; hence, it can be suggested that the biological uptake of phosphorus may be small in comparison with non-biological in this region.

5.2. Dissolved organic phosphorus

Concentration levels of dissolved organic phosphorus (DOP) both at surface and bottom are given in Table 11. Annexure 2 [Fig.25(b)] gives the representative figures of seasonal distribution of DOP. The distribution of DOP at stns. 1-9 as time series curve is incorporated in Fig. 15. The DOP values varied from 0.00 to 6.09 µg at PO_4^{3-}-P l^{-1} in the estuary. In the northern parts, between stns.1 to 4 the monsoonal values ranged from o.82 to 3.45 ug at PO_4^{3-}-P l^{-1} at surface and 1.00 to 4.78 µg at PO_4^{3-}-P l^{-1} at bottom. The values increased during postmonsoon, ranging between 0.46 and 4.41 µg at PO_4^{3-}-P l^{-1} at surface and 1.18 and 6.09 µg at PO_4^{3-}-P l^{-1} at

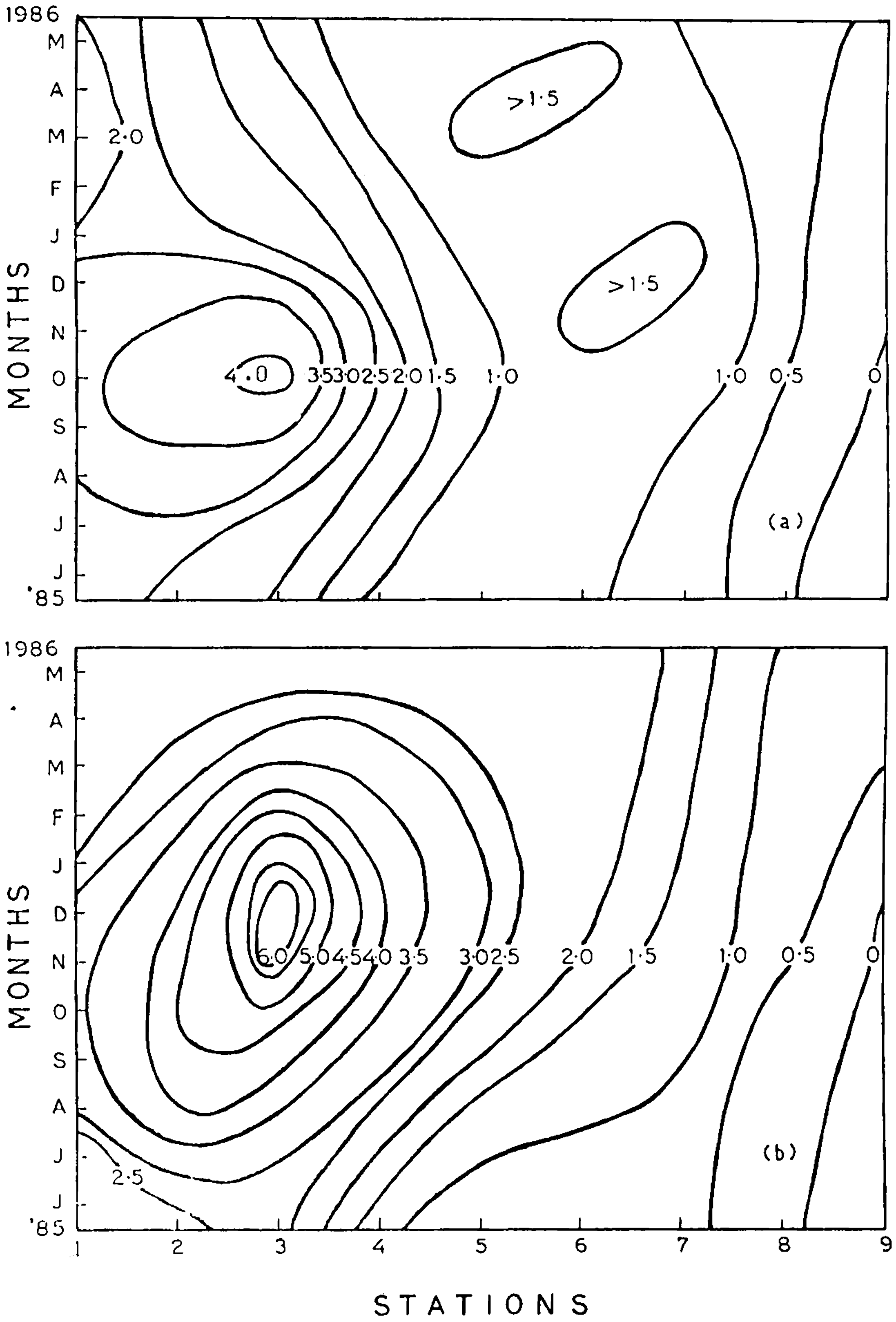


Fig. 15. Time series curve of dissolved organic phosphorus (µg at PO_4^{3-}-P l^{-1}) at surface (a) and bottom (b).

bottom. Thereafter the concentration decreased and attained low premonsoonal values ranging between 0.70 and 2.60 µg at PO_4^{3-}-P l^{-1} at surface and 1.29 and 4.36 µg at PO_4^{3-}-P l^{-1} at bottom. The highest value of phosphate was 4.41 µg at PO_4^{3-}-P l^{-1} at surface and 6.09 µg at PO_4^{3-}-P l^{-1} at bottom recorded at stn. 3 in the northern region during postmonsoon.

Chemical nature of soluble organic phosphorus compounds are complex in nature; it is suggested that the conversion of dissolved organic Phosphorous to particulate reactive phosphorus (DOP → PRP) may occur as a result of the uptake of dissolved organic compounds by bacteria and possibly by phytoplankton. The low concentration of DOP observed during monsoon may be due to the direct utilization of DOP by phytoplankton or bacteria and subsequent conversion of particulate phosphorus in the northern region. Kramer et al. (1972) concluded that dissolved organic phosphorus level may become low enough to limit the algal growth. The occurrence of low concentration of IRP (section 5.1.) and high value of particulate phosphorus (section 5.3.) in the northern region during monsoon season supports the above view.

The high DOP values during postmonsoon in the northern region may be due to the release of organic phosphorus from dead or dying organism (presumably as a result of bacterial attack) and from sediment leaching into overlying waters. Rajendran and Venugopalan (1973) have observed in Vellar estuary that concentration of DOP is comparatively high during the peak period of plankton production. This feature is attributed to the excreta from the large zooplankton community occurring during the period. Kuenzler (1970) also found that the amount of DOP excreted by different species to be responsible for the high values in the water, independent of salinity. The planktonic bloom observed during postmonsoon and large amounts of wastes discharged from fishery industry into the Cochin estuary may further support this view. It is also seen that there is a significant sharp horizontal gradient observed between stn. 3 and 4 during postmonsoon indicating the influence of a transitory period. The organic phosphorus compounds are broken down to ionic phosphorus by bacteria (Watt & Hayes, 1963). The low values of DOP observed during premonsoon period may be due to its bacterial transformation to inorganic phosphorus.

In the southern region (stns. 5-9) the concentration ranged between 0.0 and 2.18 µg at PO_4^{3-}-P l^{-1} at surface and 0.0 to 3.51 µg at PO_4^{3-}-P l^{-1} at bottom throughout the year. The higher values are recorded during postmonsoon. Bottom values are slightly higher than the surface values during all seasons. The concentration of phosphorus gradually increased from the southern tip to the Cochin barmouth. These factors indicate the law input of phosphorus (inclusive of organic) from land drainage or by river discharge.

The relationship between salinity and DOP during monsoon, postmonsoon and premonsoon both at surface and bottom are given in Fig. 16. A significant positive correlation was observed between salinity and DOP. In general, high values of phosphorus is associated with high values of salinity. During postmonsoon a wide scatter of the values is observed, indicative of the transitory postmonsoonal behaviour.

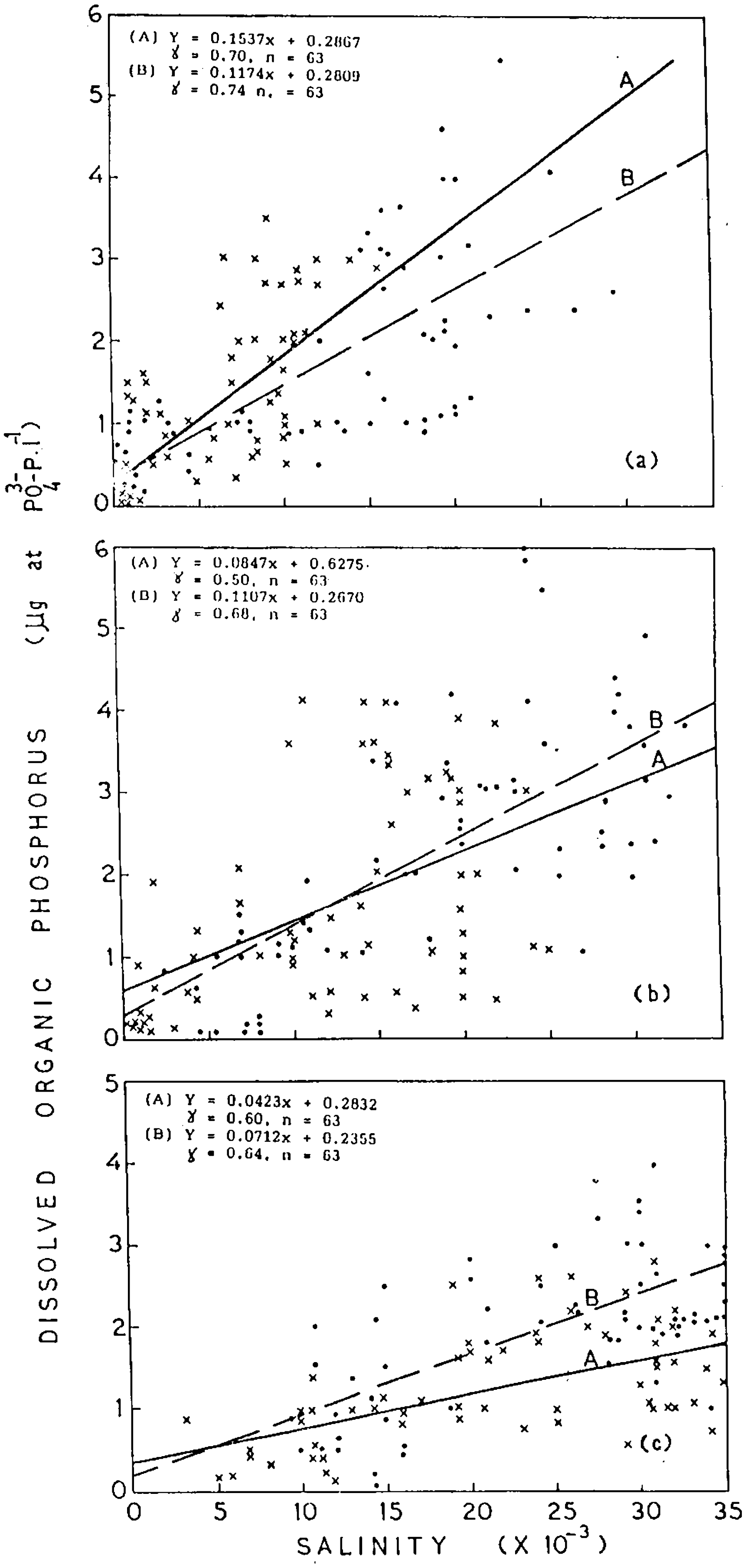


Fig. 16. Relationship between dissolved organic phosphorus and salinity during monsoon (a), postmonsoon (b) and premonsoon (c) [surface: x,

5.3. Particulate reactive phosphorus

Concentration levels of particulate reactive phosphorus (PRP) at stns. 1-9 during the period of survey are given in Table 12. Fig. 17 gives the time series curve for the distribution of PRP at these stations. Annexure 3[Fig.26(a)] gives the figures of seasonal distribution of PRP. The phosphorus fraction varies from 0.0 to 1.68 µg at PO_4^{3-}-P l^{-1} at surface and 0.0 to 2.08 µg at PO_4^{3-}-P l^{-1} at bottom. In the northern region PRP values were high during monsoon; highest values of PRP, 1.68 µg at PO_4^{3-}-P l^{-1} at surface and 2.08 µg at PO_4^{3-}-P l^{-1} at bottom were recorded between stns, 2 and 3. The values gradually decreased as season advanced to postmonsoon and premonsoon; the minimum values recorded during premonsoon range between 0.02 and 0.66 µg at PO_4^{3-}-P l^{-1} at surface and 0.0 and 0.82 µg at PO_4^{3-}-P l^{-1} at bottom. In the southern region PRP values are comparatively low and range between 0.0 and 1.12 µg at PO_4^{3-}-P l^{-1} with high values during monsoon.

The high values of PRP observed during June-July may be the result of several simultaneous processes taking place in the northern region such as (i) the conversion of DOP to PRP as a result of planktonic utilization of DOP when IRP concentrations are relatively very low (ii) precipitation and transport of particulate matter by run off and (iii) turbulant mixing of bottom waters with surface waters at shallow depths resuspending sedimented matter, thereby increasing the amount of particulate phosphorus in the northern part during monsoon. The bottom of stns. (2) and (3) where high values of PRP were recorded are covered with silty clay and clayey silt which contain large amounts of phosphate associated with organic matter. Rajendran & Venugopalan (1973) observed high PRP values in Vellar

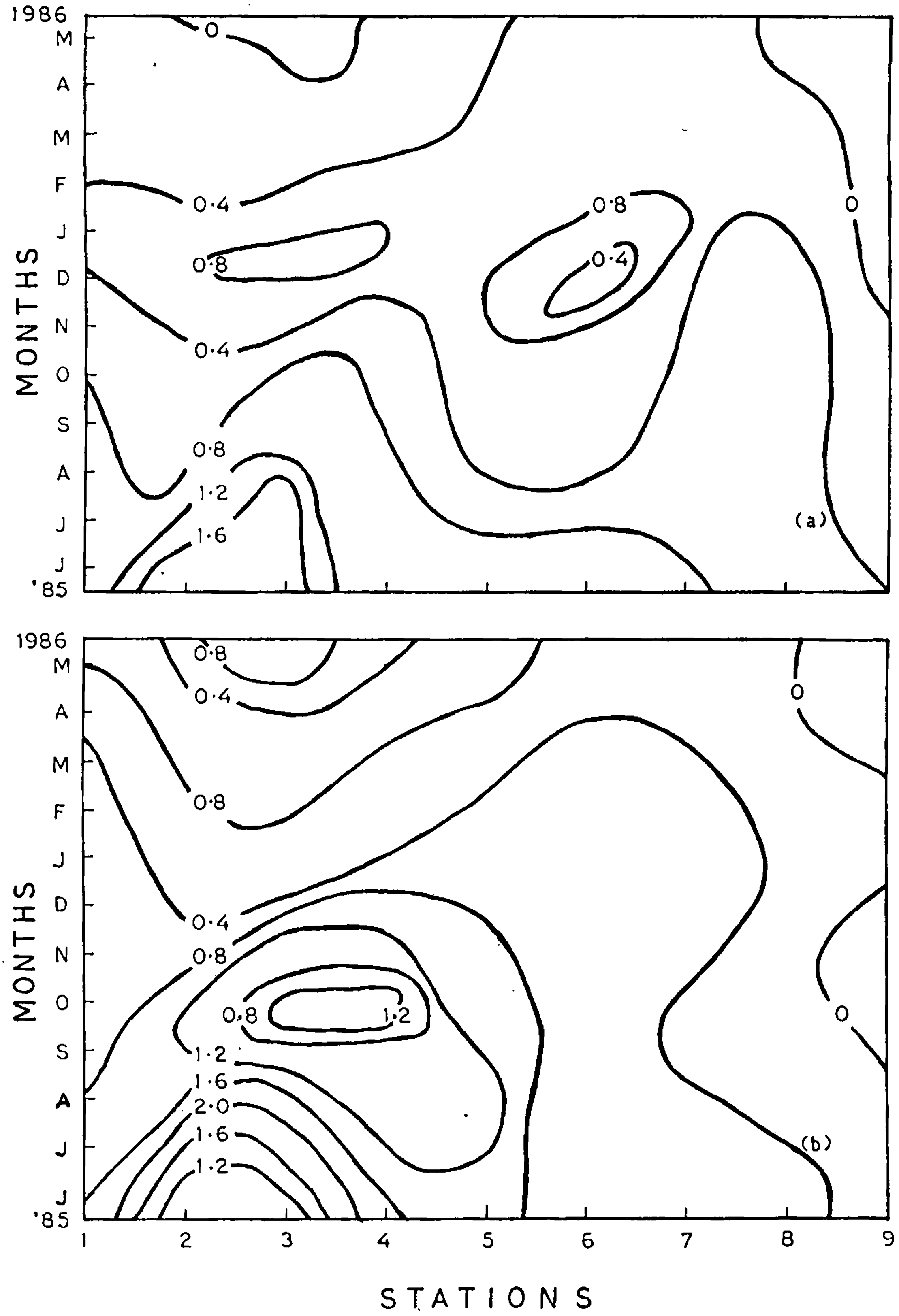


Fig. 17. Time series curve of particulate reactive phosphorus (µg at PO_4^{3-}-P l^{-1}) at surface (a) and bottom (b).

estuary attributed to the turbulant mixing and stirring-up of material, organic rich clayey silt.

In the southern region the values are very low caused by the lower influx of particulate matter and also that the estuarine bottom layer is covered with sandy material devoid of phosphate containing organic matter.

Coefficient of correlation and regression between salinity and PRP both at surface and bottom during all season were evaluated and are given as correlation diagrams in Fig. 18. No significant correlation is observed between salinity and PRP.

5.4. **Total reactive phosphorus**

Table 13 gives the concentration level of total reactive phosphorus (TRP) both at surface and bottom of all stations during the period of survey. The distribution of TRP both at surface and bottom during survey as time series curves are given in Fig. 19. Annexure 3 [Fig.26(b)] gives the representative figures of seasonal distribution of TRP. The values range widely from 0.00 to 18.40 µg at PO_4^{3-}-P l^{-1}. In the northern region the monsoonal TRP values range between 1.19 and 8.35 µg at PO_4^{3-}-P l^{-1} at surface and between 2.90 and 8.48 µg at PO_4^{3-}-P l^{-1} at bottom gradually increasing as season advanced to postmonsoon and premonsoon. The values observed during premonsoon ranged from 2.08 to 14.30 µg at PO_4^{3-}-P l^{-1} at surface and from 4.87 to 18.40 µg at PO_4^{3-}-P l^{-1} at bottom. The maximum TRP concentration observed at stn. 3 is 18.40 µg at PO_4^{3-}-P l^{-1}. In the southern region the monsoonal values ranged from 0.00 to 4.94 µg at PO_4^{3-}-P l^{-1} at surface to 0.00 to 5.24 µg at PO_4^{3-}-P l^{-1} at bottom. The premonsoonal

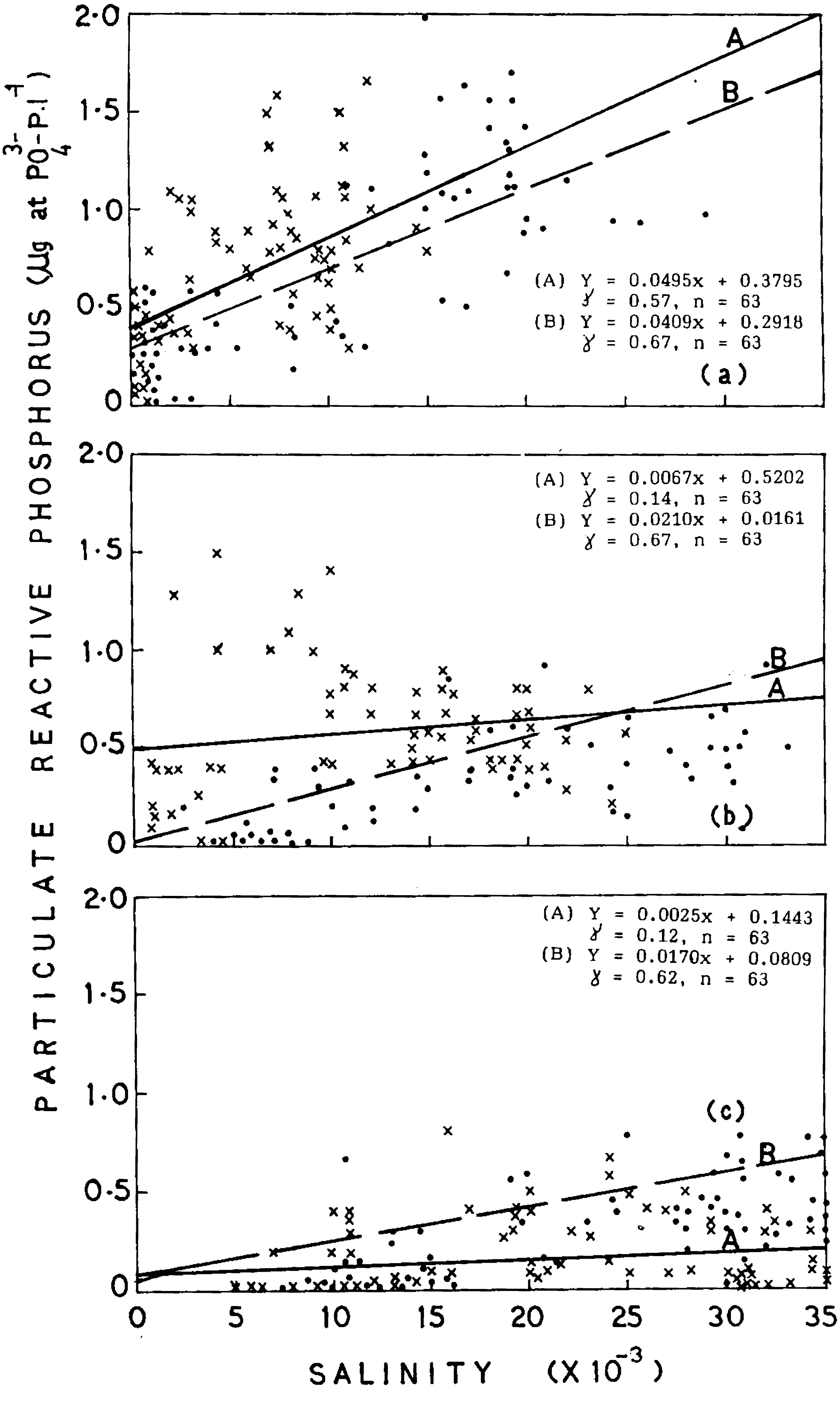


Fig. 18. Relationship between particulate reactive phosphorus and salinity during monsoon (a), postmonsoon (b) and premonsoon (c) [surface: x, line - A; bottom: • , line - B].

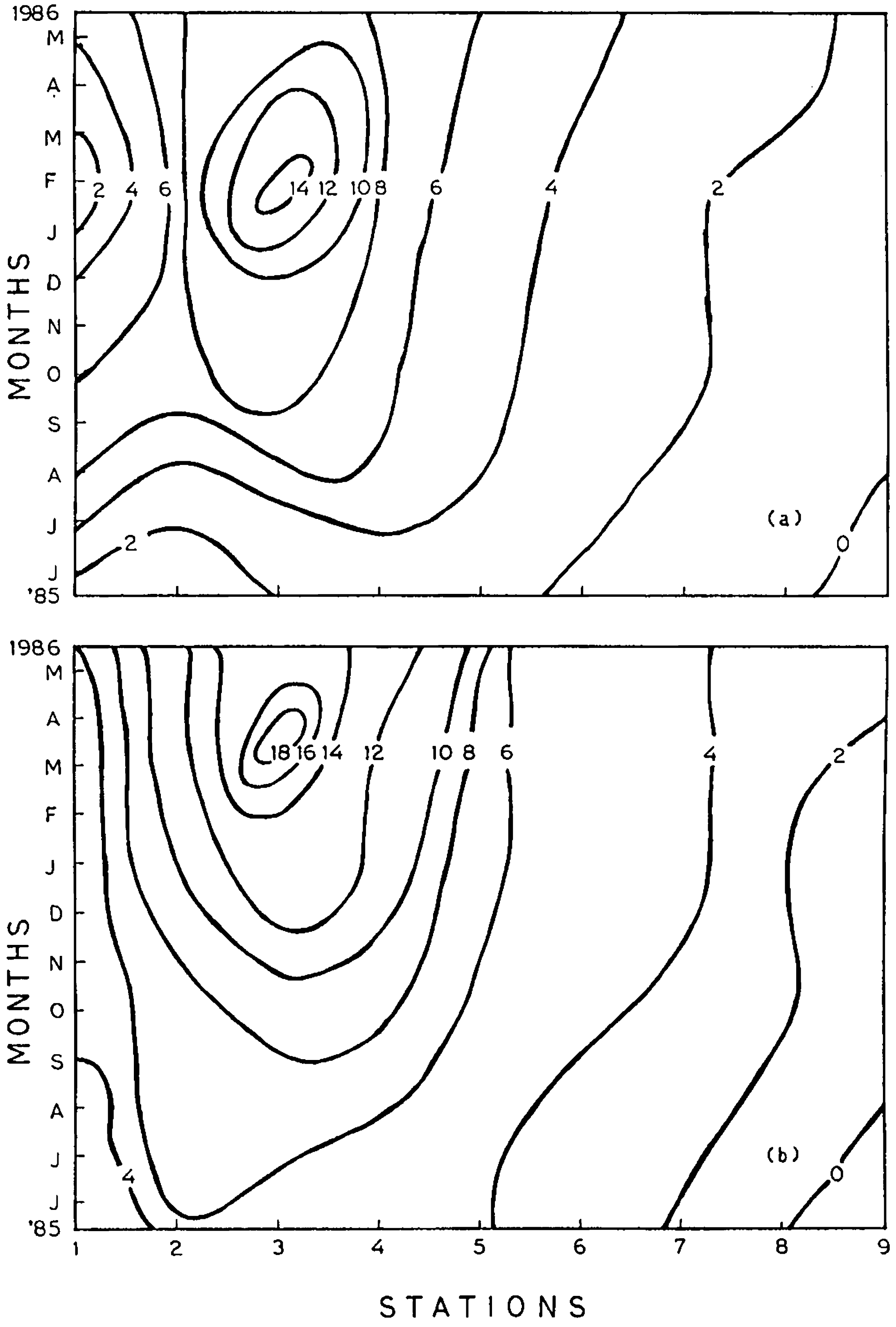


Fig. 19. Time series curve of total reactive phosphorus (μg at PO_4^{3-}-P l^{-1}) at surface (a) and bottom (b).

values ranged between 0.76 and 5.66 µg at PO_4^{3-}-P l^{-1} at surface and 0.68 and 7.11 µg at PO_4^{3-}-P l^{-1} at bottom. The phosphorus level showed a gradual decrease from barmouth to the southern tip of the estuary. A horizontal gradient was observed in the northern region during premonsoon.

The low values recorded in July (monsoon) is attributed to the excessive rainfall in this month (180 cm) resulting in low salinity, lower pH and high concentration of DO which are conditions favourable for the removal of phosphorus from the overlying water by the suspended solid load. Jitts (1959) showed that estuarine sediment can trap 80-90% of phosphate during the period of high runoff which might be released under favourable conditions. Studies on sediment associated phosphorus such as adsorbed and interstitial phosphate (section 5.5), reveal higher values during monsoon. Thus the low value of TRP observed during this period is due to the adsorption of IRP, a fraction of TRP, from overlying water by sediments. Again low values of TRP observed during monsoon months showed that terrestrial run off does not contribute significant amount of phosphorus to the estuary. A characteristic feature observed is that both TRP and IRP exhibited almost similar seasonal variations. The monsoonal values of TRP gradually increase during postmonsoon and this increase is due to the increase of DOP, another fraction of TRP associated with the phytoplanktonic bloom during this period.

The high values of TRP during premonsoon in the northern region is associated with high values of IRP and hence the increase of TRP is caused by the influx of industrial effluents and land drainage to this areas. The high values of TRP again corresponds with high values of salinity and lower values of DO during this period. The desorption and release of phosphorus from sediment during premonsoon may also contribute to the increase of TRP of the overlying water. Adsorbed and interstitial phosphorus of the sediments (section 5.5.2 & 3) are found to be very low during this period.

The coefficient of correlation and regression of TRP and IRP were also calculated. An important feature observed from the composite correlation diagram (Fig. 20) between IRP and TRP during premonsoon is the perfect linearity with a γ value of 0.94.

5.5. **Sediment Analysis**

5.5.1. Textural characteristics

Textural characteristics of the sediment play a significant role on the distribution and concentration of phosphate both in sediment and overlying water column. A study of textural analysis was therefore undertaken to determine whether phosphate - sediment interactions might have to be considered when predicting the environmental effects of increased phosphorus loads in the estuary.

Table 14 gives the composition of sand, silt, clay and moisture content (weight percentage) of the sediment at each station along with station depth during different seasons, calculated by averaging the monthly data. The study area is designated based on the sediment type according to Shepard's (1954) classification as given in the table where sand is composed of particles greater than 63 μ, silt lies between 63 to 4 μ and those particles less than 4 μ being termed as clay. The composition of sediment varies markedly from place to place, however, the seasonal variation at each station is minimal.

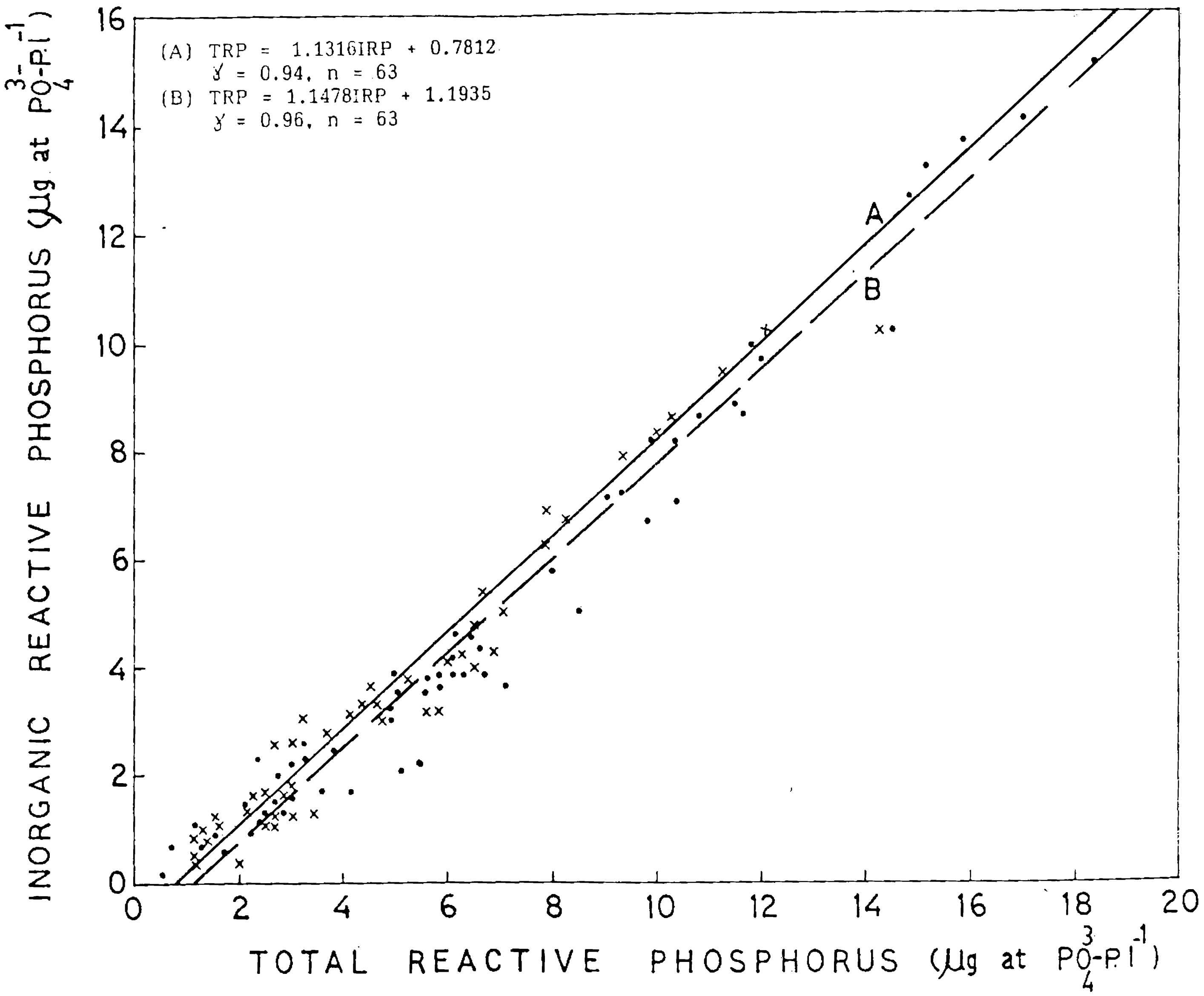


Fig. 20. Relationship between total reactive phosphorus and inorganic reactive phosphorus during premonsoon (surface: x, line - A; bottom: ● , line - B.)

At the northern-most part of the estuary (stn. 1) where the northern branch of Periyar river joins the estuary the main constituent fraction in the sediment was sand with negligible amount of clay and silt and with low amount of moisture ($\leq$ 33%). This is in agreement with the earlier findings of Josanto (1971) that the northern part of the estuary near Azhikode is characterized by a sandy zone. Even after 16 years of changes in the hydrological condition and deforestation in catchment areas of the river the sediment texture does not appear to have changed. Along the middle region of the northern parts (stns. 2 & 3), the sediment was found to be of silty clay and clayey silt nature respectively, characterized by very low sand contents varying from 3.0 to 7.5%. Stn.3 recorded a maximum value of silt content 58.3% associated with high percentage of moisture (71%) during the monsoon season. This might be due to the increased siltation in this region.

The Cochin harbour area (stns. 4 & 5) was predominantly covered with silty clay. The rest of the estuary on the southern part (stns. 6 to 9) had a substratum of clayey sand. The sand content in the sediment varied widely from 20% to 75% with high values towards the southern region. This may be interpreted as due to the reduced displacement rate of coarse sand and large transport of silt and clay by river flow from the southern region towards barmouth. The downstream mobility of fine sediment is indicated by the decreasing tendency in the percentage of silt and clay towards the southern part.

5.5.2. NaCl leached (interstitial) phosphorus

The concentration level of interstitial phosphorus in the sediments is given in Table 15. The distribution pattern of interstitial phosphorus is presented in Fig. 21(a). Annexure 4 [Fig.27(a)] gives the representative figures of seasonal distribution of interstitial phosphorus. High values were recorded in the northern regions varying over a wide range from 9.81 to 51.13 µg at PO_4^{3-}-P g^{-1} wet mud. The highest value (51.13 µg at PO_4^{3-}-P g^{-1}) was observed at stn. 3 during monsoon and was associated with high percentage of silt (58.3%) and moisture (71%). Stns. 2, 4 & 5 recorded nearly similar values around 35.0 µg at PO_4^{3-}-P g^{-1} during monsoon. These high monsoonal values steadily decreased and attained a minimum value of 15.0 µg at PO_4^{3-}--P g^{-1} during premonsoon. Silt content also gradually decreased at all stations during this period. Stn. 1 which is predominantly covered with sand recorded slightly lower values (20.0 µg at PO_4^{3-}-P g^{-1}) with negligible amount of silt during monsoon. The values decreased as the season advanced to postmonsoon and premonsoon and attained the lowest value of 9.81 µg at PO_4^{3-}-P g^{-1} during premonsoon.

In the southern region the interstitial phosphorus ranged between 9.99 and 30.66 µg at PO_4^{3-}-P g^{-1}. Relatively lower values around (15.0 - 20.0 µg at PO_4^{3-}-P g^{-1}) were observed during monsoon and was associated with low percentage of silt and moisture. The values increased to $\simeq$25.0 µg at PO_4^{3-}-P g^{-1} during postmonsoon with increase in salinity. Thereafter the values decreased in the range of 15.0 to 20.0 µg at PO_4^{3-}-P g^{-1} during premonsoon. It is observed that the southern part of the estuary recorded the same value of interstitial phosphorus both during monsoon and premonsoon period.

5.5.3. NaOH leached (adsorbed) phosphorus

Table 15 gives the concentration level of adsorbed phosphorus during the period of survey. Primarily, from the distribution pattern, it is observed that adsorbed phosphorus contents (Fig. 21(b) are higher than interstitial phosphorus at stations on the northern parts round the year. Annexure 4 [Fig.27(b)] gives the representative figures of seasonal distribution of adsorbed phosphorus. The distribution behaviour of adsorbed phosphorus is very much similar to interstitial phosphorus. The northern region recorded higher values ranging from 7.77 to 75.13 µg at PO_4^{3-}-P g^{-1} wet mud. The highest value (75.13 µg at PO_4^{3-}-P g^{-1} recorded at stn. 3 during monsoon was again associated with high percentage of silt (58.3%) and a low salinity (14-18 x 10^{-3}) of overlying water. Stns.2 & 4 recorded the same value (45.0 - 60.0 µg at PO_4^{3-}-P g^{-1}) of adsorbed phosphorus during monsoon with silt content of 45.4 and 39.5% respectively. During this period the inorganic reactive phosphorus (IRP) of overlying water was very low ranging between 3 and 5 µg at PO_4^{3-}-P l^{-1} with DO values ranging between 5.5 and 6.5 ml l^{-1}. The high values of adsorbed phosphorus observed during monsoon steadily decreased and reached low values of 20-30 µg at PO_4^{3-}-P g^{-1}, as the season advanced to postmonsoon and premonsoon. During this period salinity of overlying water also increased and reached a maximum value of 34 x 10^{-3}. However, the DO value decreased to 3.5 ml l^{-1} during this period. Inorganic reactive phosphorus of overlying water was higher, ranging between 6 and 15 µg at PO_4^{3-}-P l^{-1}.

During monsoon in the southern region, adsorbed phosphorus level ranged between 15.0 and 45.0 µg at PO_4^{3-}-P g^{-1} with slight overall increase during postmonsoon. As the season advanced to premonsoon the adsorbed phosphorus values dropped sharply.

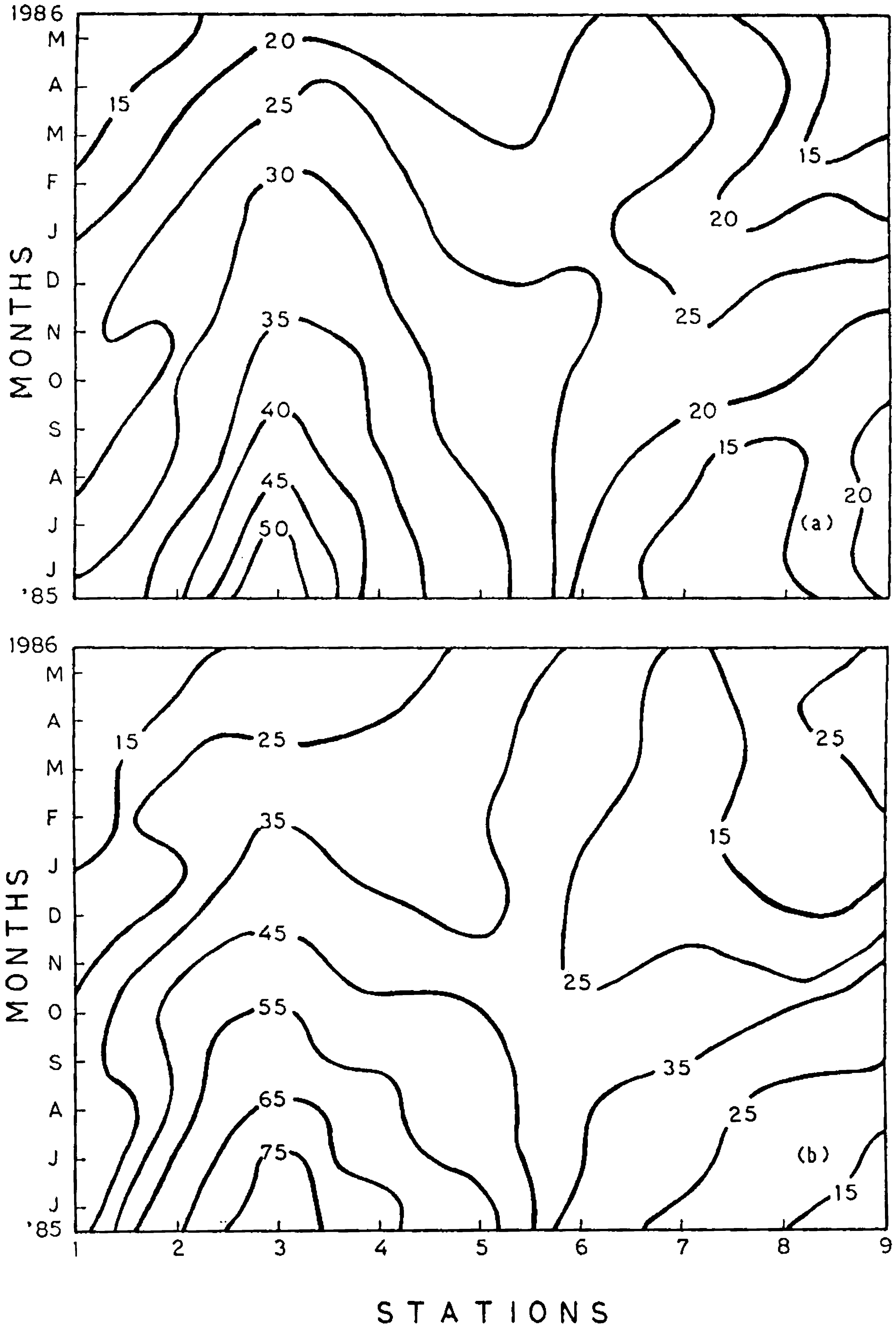


Fig. 21. Time series curve of interstitial (a) and adsorbed (b) sediment phosphorus (μg at PO_4^{3-}-P g^{-1}).

Reddy & Sankaranarayanan (1972) observed that adsorptive tendency is high with higher silt percentage in sediments and that low silt content with higher percentage of fine sand appears to be conducive for active regeneration. Pomeroy et al. (1965) report that low salinity and high DO conditions favour adsorption of phosphorus from overlying water to sediment. The present investigation showed that high values of interstitial and adsorbed phosphorus recorded during monsoon in the middle of the northern part of the estuary are also associated with high percentage of silt. The salinity values of 14-18 x 10^{-3} and DO values of 5.5 - 6.5 ml l^{-1} observed during this period may favour adsorption. During monsoon the permeability of the sediment is very low because of high silt content, resulting in the retention of large quantities of phosphate into sediment interstices and consequently the overlying water has a low concentration of phosphate. The earlier studies conducted by several authors (Murty & Veerayya, 1972; Ansari & Rajagopal, 1974) in the Cochin backwaters also reported high phosphate concentration in areas with a higher proportion of silt and clay content in the sediment. It is concluded that there exists a relationship between phosphorus content and the texture of the sediment in the estuary in which there is an increase of phosphorus content with increase in silt/clay content of sediment.

The high values of interstitial and adsorbed phosphorus during monsoon in the northern region steadily decreased and attained a minimum value during premonsoon. This is attributed to the release of phosphorus from the sediment to the overlying water (15.61 µg at PO_4^{3-}-P l^{-1}). Reddy & Sankaranarayanan (1972) have shown that the bacterial activity and physicochemical composition of the sediment at different sites attributed to difference in the release of phosphorus.

The low oxygen content and continuous increase of phosphorus concentration of the overlying water indicate a possible high microbial activity at the mud-water interface. Further, it has been shown that the increased salinity and low dissolved oxygen of overlying water enhance the release of phosphorus from sediment to overlying water (Carritt & Goodgal, 1954; Burns & Salomon, 1969;, Mortimer, 1971; Stirling & Wormald, 1977). The present study reveals that increase of salinity from 14-18 x 10^{-3} to 34 x 10^{-3} and reduction of DO to 3.5 ml l^{-1} favour the desorption of phosphorus from sediments. The high value of inorganic reactive phosphorus (IRP) of overlying water observed during premonsoon in the northern region (section 5.1) is partly due to the release of phosphorus from the sediment to the overlying water.

The southern part of the estuary recorded generally low values of phosphorus without any marked seasonal variation. Again, it is observed that low values of interstitial and adsorbed phosphorus recorded in this region is characterized by clayey sand, with high amount of sand content. Coarseness of the sand allows no possibility of retention of any phosphorus in the interstices of the sediment. Furthermore, hydrographic chemistry of the overlying water does not have any significant influence on the bacterial regenerative activity and consequently sediment-water interaction is not a governing factor on the distribution and concentration of phosphorus in the sediments of the southern part of the estuary.

The variation of pH values (both seasonal and spatial) observed during the investigation indicate that it does not have relatively any significant role on the exchange of phosphorus between the sediment and overlying water.

CHAPTER 6

DISSOLVED SILICON IN THE ESTUARY

6.1. Inorganic reactive silicate - silicon

Silicon is a biologically essential nutrient to marine organisms like diatoms, radiolarians and sponges for their growth and the formation of their skeletal materials. The uptake of silicon by the growing phytoplankton population results in the depletion of the silicon content of the seawater. However, when these siliceous organisms die and disintegrate, silicon is rapidly liberated into the seawater and the concentration of silicon increases. Thus, as a consequence of its biological significance, silicon exhibits a strong seasonal dependence reflecting the waxing and waning of the life processes. Silicon can also be used as an important chemical tool in oceanography since the wide variability of its concentration could be used for tracing water masses in the seas (Richards, 1958).

It is well known that silicates in river waters are the chief source of silica to the marine environment. Livingstone (1963) compiled the values of the silica content of numerous rivers of the world and estimated that rivers supply up to 4.25×10^{14}g SiO_2 yr^{-1} to the oceans. The submarine volcanism and associated hydrothermal emanations act as a subordinate source of silica to the marine environment; Calvert (1968) estimated the flux of silica from these sources to be

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The terms silicon, silica, and silicates are more or less synonymously used, however, the concentration is given as µg at (silicate-silicon) l^{-1}

3×10^{10}g SiO_2 yr^{-1}. Dissolution from suspended particles, bottom sediments and rocks may yet be another source of silica to the environment; recently Warnke (1970) and Hurd (1973) estimated the magnitude of these inputs to be 2×10^{12}g SiO_2 yr^{-1}. The total flux of dissolved silica to the marine environment was reported as $6.1 \pm 1.8 \times 10^{14}$g SiO_2 yr^{-1} by Demaster (1981).

Silicon is present mainly in two forms in natural waters: (i) dissolved and (ii) particulate derived from the weathering of silicate rocks. The dissolved silicon exists largely as orthosilicic acid, H_4SiO_4 (Siever, 1971). A small fraction (about 5%) of the dissolved silicon exists in the dissociated form (at pH 8) as indicated by the values of the first and second dissociation constants (3.90×10^{-10} and 1.95×10^{-13} respectively). However, there is a difference of opinion about the existance of other forms of silicon (polymerized) in either river water or seawater (Burton *et al.*, 1970; Siever, 1971).

Particulate silicon is again found in two forms: biogenic (such as diatom frustules) and non-biogenic. It is well known that particulate silicon minerals have a profound effect on regulating the pH of the seawater (Mackenzie *et al.*, 1967). A pH dependent ion-exchange equilibrium between solution and particulate silicon minerals according to equation

$$3Al_2Si_2O_5(OH) + 4SiO_2 + 2K^+ + 2Ca^+ + 18H_2O \rightleftharpoons 2KCaAl_3Si_5O_{16}(H_2O)_6 + 15H^+ \qquad (6.1.)$$

is the major buffering system in oceans. Sillen (1961) has estimated the buffering capacity of the silicates to be about 2000 times the buffering capacity of the carbonate system.

The concentrations of silica within water bodies frequently exhibit marked variation in seasonal and spatial distribution. The typical range of silica content in natural waters is about 1 to 140 mg SiO_2 l^{-1}; some brackish waters contain very high amounts ($\geq$ 1100 mg l^{-1}). High concentrations are found in ground water in contact with volcanic rocks and low amounts of silicate in water, associated with carbonate rocks. High silica content in water is undesirable for a number of industrial uses because of silicate scales formed on the equipment, particularly on high pressure steam - turbine blades.

River transport is one of the factors influencing the variations in concentration of silicon in the marine environment. The physical properties such as temperature and solubility of certain minerals (eg. hydroxylated magnesium silicate) also have a significant influence on the variation of silicon concentration. Martin (1970) reported that the suspended clay minerals in streams release silicon to silica - deficient seawater (dissolved silica concentration $<$ 3 mg l^{-1}) or remove silica from silica-enriched seawater (dissolved silica concentration $>$25 mg l^{-1}). The interstitial waters of marine sediments generally contain more dissolved silicon than the overlying seawater, so that concentration gradient will drive a diffusive flux of silicon from sediment to water (Harriss, 1967).

One of the topic of considerable interest in estuarine chemistry is the wide change in the dissolved silica concentration during estuarine mixing. It has long been thought that silica might be removed from silica rich river water as it mixes with seawater in the estuarine zone; the mechanism of removal reviewed by Burton *et al*. (1970), Liss (1976) and Aston (1978). Krauskopf (1956) suggested that during the mixing of river water with seawater in estuaries, the increased electrolytic concentration leads to the formation of polymeric and colloidal forms of silicic acid which flocculate resulting in the removal of dissolved silica.

The amount of silica removal in estuaries has been estimated by numerous authors by the method based on dissolved silica versus salinity plots (Liss, 1976). By this method it has been suggested that the silica removal process occurs within an estuary, when the data points lies below the predicted dilution line. Kamatani & Takano (1984) suggested that the above technique of plots of dissolved silica versus salinity, only gives an indication of apparent removal process. They also concluded that the removal processes may be influenced by the formation of biogenic silica, variation in the amount of fresh water input, and the activity of diatoms. However, DeMaster (1981) computed the amount of silica removal in the estuarine environment by comparing the amount of silica supplied to the oceans by rivers with total amount of terrigenous materials carried by rivers.

The field and experimental data on dissolved silica obtained to date, suggest that removal processes are limited to a few percentage extending to a maximum value of 30% (Morris et al, 1981). The study carried out by Wollast (1973 & 1978) in laboratory as well as in the Scheldt estuary concluded that silica removal in estuaries can occur only when the concentration of dissolved silica in the water is greater than 14 mg SiO_2 l^{-1}.

The work in several Japanese estuaries (Maeda & Tsukamoto, 1959; Maeda & Takesue, 1961) suggested that there is a linear relationship between dissolved silicon concentration and the salinity of

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the water. Burton et al. (1970) have studied the distribution and behaviour of dissolved silicon in the Southampton waters, and again observed a linear inverse relationship between salinity and silicon concentration. A series of papers by Peterson and his co-workers (1975 a & b, 1978) and Conomos (1979) on dissolved silicon have contributed greatly to our knowledge of the behaviour of dissolved silica in San Francisco Bay. Non-conservative behaviour of dissolved silica can be interpreted primarily due to biological production and degradation processes. Milliman & Boyle (1975) have also suggested that biological processes are important in controlling the concentration and distribution of silica in estuarine waters. Bien et al. (1958) and Liss & Spencer (1970) however have concluded that apart from biological uptake, non-biological removal of silicon by inorganic precipitation also contributes to the control of distribution of silica in the estuary. Siever & Woodford (1973) reported that when overlying water is deficient in silicon, desorption of silicon from suspended minerals take place and vice versa leading to maintain an equilibrium concentration. Callaway & Specht (1982) have summarized the nature of the distribution of dissolved silica with respect to season, run off and other parameters in the Yaquina, a small Oregon coastal plain estuary. They have suggested that non-conservative behaviour of silica can be attributed to the increase of phytoplankton population during low run off. They also pointed out the importance of residence time as a controlling factor which help to determine whether the longitudinal distribution of silica is conservative or non-conservative. Thus it may be suggested that the behaviour of silicon in estuarine environment is governed by the result of physical, chemical and biological processes taking place which vary from one estuary to another.

bution of dissolved silica in the Indian estuaries of tropical region, the variation in dissolved silica with respect to seasons and causes thereof have not so far been critically analysed. Studies on the behaviour of dissolved silicon in Mandovi - Zuari river estuarine system was conducted by DeSousa (1983) who concluded that it behaves non-conservatively; the great loss in the low salinity region is probably due to adsorption on suspended solids. Purushothaman & Venugopalan (1972) reported that distribution of dissolved silicon in the Vellar estuary is governed not only by a simple dilution process but also by factors such as the removal of silicon by inorganic precipitation. The behaviour of silicate content in the Cochin estuary studied by Joseph (1974), is related to phytoplankton bloom. The present work devotes attention on the seasonal distribution of dissolved silicon in the Cochin estuary and attempts to characterize its estuarine behaviour.

6.1. Inorganic reactive silicate - silicon

The data on inorganic reactive silicate - silicon (RSi) at all stations are shown in Table 16. Distribution patterns of RSi at both surface and bottom waters are given in Fig. 22. Annexure 5 (Fig.28) gives the figures of representative seasonal distribution of RSi. The longitudinal variation of RSi shows a well defined pattern:high concentrations were recorded in the freshwater regions with gradual seaward decrease. RSi values ranged from 28.20 µg at SiO_4^{4-}- Si l^{-1} in the northern region to 182.30 µg at Si l^{-1} in the southern region of the estuary. A noteworthy feature of the RSi distribution in the estuary is the seasonal decrease of silicate content during the period of survey ie. from June 1985 (monsoon) to May 1986 (premonsoon). However, further studies conducted in Cochin estuary from June 1986

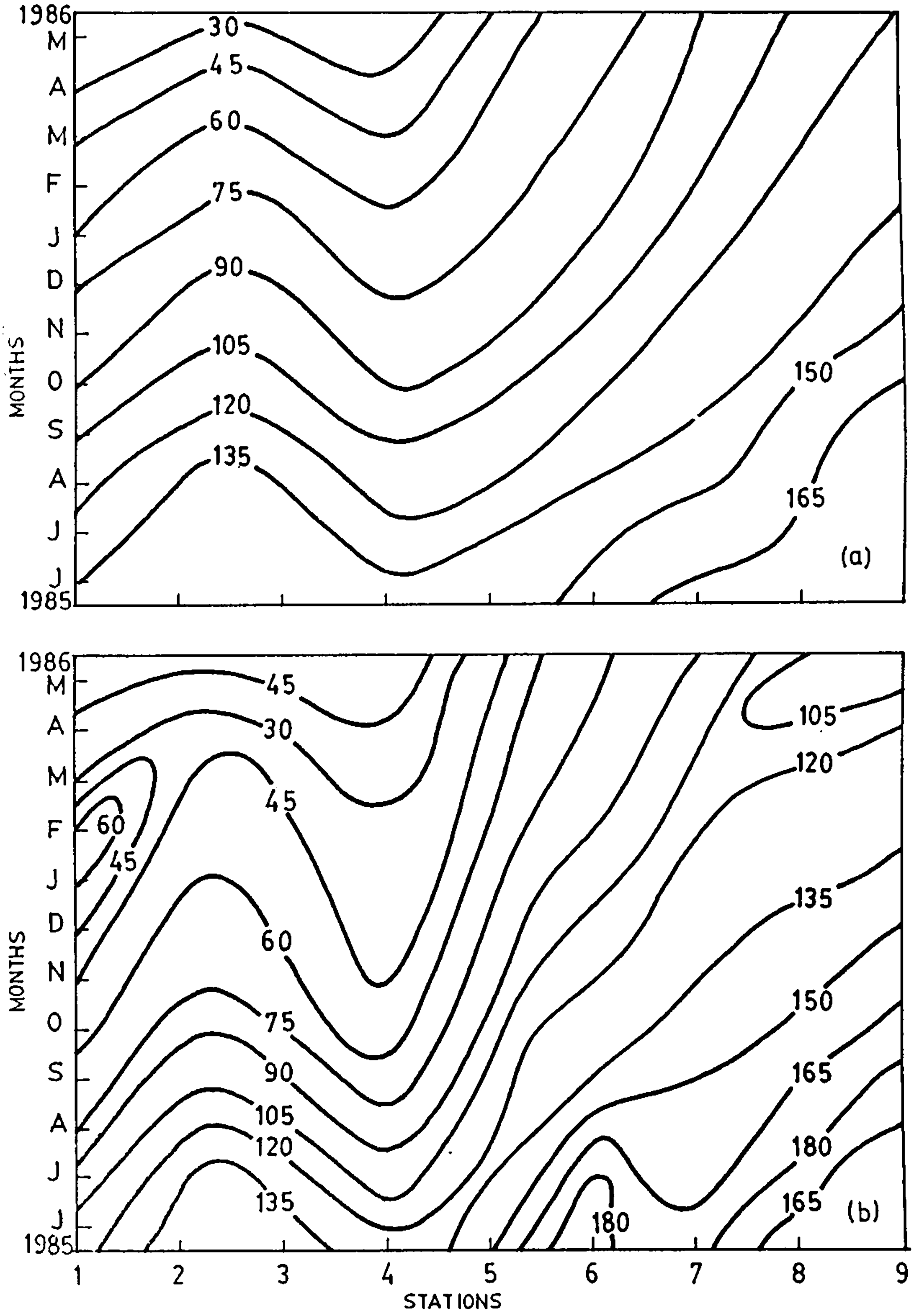

Fig. 22. Time series curve of inorganic reactive silicate-silicon (μg at SiO_4^{4-}-Si l^{-1}) at surface (a) and bottom (b).

to September 1986 (monsoon) showed that the above low premonsoonal values increased and again attained a maximum (185.30 µg at SiO_4^{4-}-Si l^{-1}) in July 1986. (unpublished data, Anirudhan, 1987).

The observed spatial and seasonal decrease of RSi indicated that silicate contribution in the estuary is largely dependent on external sources such as river water discharge and land drainage. An examination of the overall distribution characteristics of RSi in the estuary reveals that silicate concentration and isohaline pattern are in unison; however, the distribution of concentration values are dissimilar. This clearly suggests that the region under study is affected by the intrusion of seawater which is also a decisive factor controlling the distribution of reactive silicate in the estuary.

In the northern regions monsoonal values (100-140 µg at SiO_4^{4-}-Si l^{-1} at surface and 60 - 135 µg at SiO_4^{4-}- Si l^{-1} at bottom) decrease as the season progresses to postmonsoon and premonsoon. At all times, stns. 1 & 4 recorded almost the same values of silicate with stns. 2 & 3 recording slightly higher values. The influence of seawater at stns. 1 & 4 and subsequent mixing with river water largely influence the distribution of silicon on the northern part of the estuary. The high RSi content observed during monsoon months may be due to the discharge of large volumes of silt-laden freshwater into the estuary by rivers.

The lower values observed during premonsoon in the northern region was associated with high salinity (32-35 x 10^{-3}) and low dissolved oxygen (DO $<$ 3.5 ml l^{-1}). This is ascribed to low influx of river water and large scale penetration of saline waters. The earlier study conducted by Joseph (1974) also reported low values of reactive silicate during premonsoon in the northern region. The present investigation also shows low values of reactive silicate during premonsoon associated with low content of silt (see section 5.5.1.). Removal of silicate by flocculation through increased electrolytic concentration during the mixing of seawater with river water may also contribute to the low values of reactive silicate during premonsoon in the northern region.

The higher values of RSi (120 - 182 µg at SiO_4^{4-}- Si l^{-1}) was recorded on the southern region during monsoon. This is caused by high land drainage of silicate rich water influxing into the estuary, as a result of runoff. With the onset of monsoon, high values of RSi was observed in the southern parts was consistently associated with low values of salinity (0-11 x 10^{-3}) and high values of DO (7 - 8.5 ml l^{-1}); this shows the direct transport of RSi to the barmouth region (without appreciable removal in the estuary). As the season advances to postmonsoon and premonsoon, decrease in RSi is observed which is inversely related to salinity.

As observed in the case of salinity distribution during the period of survey, the silicate values also exhibited a transitional behaviour during postmonsoon season. The freshwater inputs are in the range of 60 - 135 µg at SiO_4^{4-}- Si l^{-1} into the estuary during the period. Postmonsoon season has been observed to be a period of active biological production involving the utilization of available nutrients in this estuary (Wyatt & Qasim, 1973; Gupta & Pylee, 1964).

Coefficient of correlation and regression equations between salinity and RSi are given in Fig. 23 for the three seasons. The present study shows a significant negative correlation between salinity

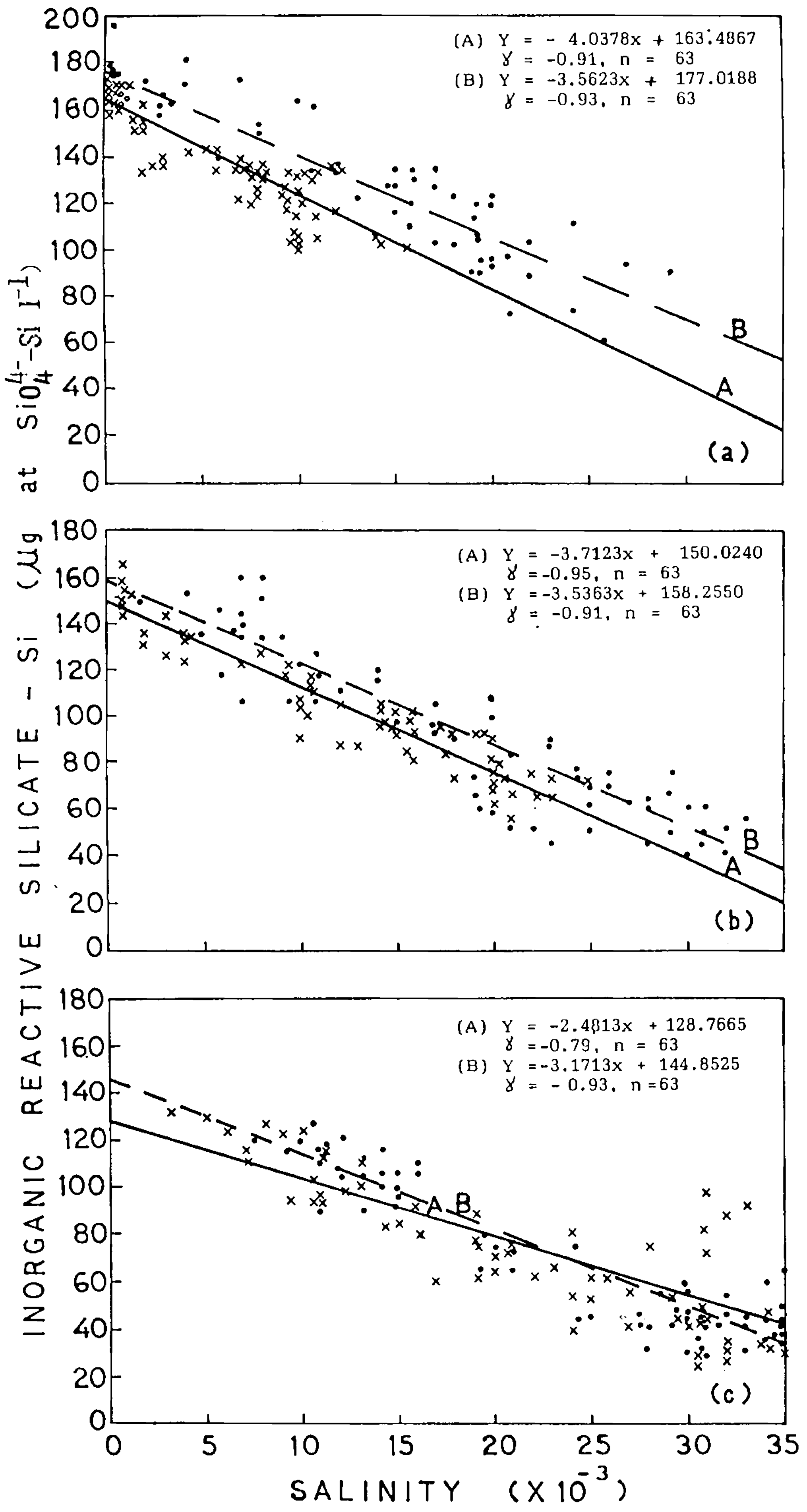

Fig. 23. Relationship between reactive silicate-silicon

and RSi during all seasons, showing that silicate behaves conservatively in this estuary. Studies on the distribution of silicate in the lower reaches of Periyar river (Anirudhan et al., 1987; Nambisan & Anirudhan, 1987) indicated high concentration at the river end which decreased gradually downstream with low values at the seaward end in conformity with the pattern found in most of the other estuaries. This study further substantiated the already observed conservative behaviour of silicate in this estuary.

Thus, the results of the present investigation show that the silicate behaviour in the Cochin estuary is characterized by seasonal variations as well as the hydrological setting. The transport of silicate rich freshwater across the boundaries of the estuary, abstaining most removal processes turn out to be a marked feature for the southern parts of the Cochin estuary during monsoon months. There is, however, active removal of silica during non-monsoonal seasons.

SUMMARY

The study focuses attention on the nutrient chemistry of a tropical estuary, namely, the Cochin estuary. The investigation was planned with the objective of studying the estuarine nutrient behaviour and to assess the role of biogeochemical cycling. The distribution of parameters of interest are better explained in the light of the hydrography of the region. Largely associated with the pollution problems of Cochin estuary receiving industrial and domestic wastes, this thesis projects the role of environmental parameters modifying the nutrient content of the water body coupled with studies on their minute variability subjected to physical, chemical and biological processes.

The study has incorporated parameters like temperature, salinity, pH and DO; nutrients were investigated by the study of nitrite, nitrate, ammonia, inorganic reactive phosphorus, dissolved organic phosphorus, particulate reactive phosphorus, total reactive phosphorus and inorganic reactive silicate-silicon at surface and bottom layers of the estuary. Sediment associated interstitial and adsorbed phosphorus for a period of one year (1985-1986) were also incorporated. Results are discussed with the aid of time series curves. The salient features of the study are summarized as follows.

The hydrographical features of the Cochin estuary is subjected to great many seasonal changes influenced by influx of river water and tidal intrusion of seawater. The seasonal variation of temperature observed within the estuary was mainly due to the climatic setting

for this tropical region; the variations were more pronounced in the northern regions than the southern regions. A vertical gradient in temperature was incidently observed on the northern parts whereas the southern regions experience greater vertical mixing. The salinity distribution in this estuary has three well marked features: (i) stratification observed at the Cochin barmouth region is governed by the continuous supply of freshwater at surface and seawater along the bottom layers (ii) the hydrographical features on the northern parts are largely controlled by seawater intrusion through Cochin barmouth, exhibiting features of a partially mixed estuary (iii) the vast expanse on the southern parts of the estuary are observed to be better mixed in the vertical. The salinity distribution, however, has strong seasonal variability coinciding with the onset and withdrawal of southwest monsoon.

The estuarine waters record pH on the alkaline side with pronounced seasonal variations. Higher values of pH during postmonsoon is attributed to the excessive photosynthetic activity; again, the northern regions exhibit higher values than the southern parts. With the relative decrease of seawater influence, the pH values also decrease from the barmouth region to the southern parts of the estuary. The high monsoonal values of dissolved oxygen observed on the northern region gradually decreases as the season advances to premonsoon. High monsoonal values are due to the highly oxygenated rain waters and the lowering of oxygen content, due to effluents discharged from fishery industries of this region during premonsoon. This study has not encountered values of oxygen very very low to ascribe anoxic conditions within the estuary, but has observed instantaneous low content at badly polluted sites.

The important aspects of the studies on the distribution and seasonal variations of nitrogenous nutrients in the Cochin estuary are interpreted on the basis of general hydrographical conditions, various geochemical processes and discharge of domestic and industrial effluents. Regressional behaviour between nitrogenous nutrients and salinity and their interrelationship are evaluated in order to establish the estuarine fate of the above nutrients. A prominent feature of nitrite - nitrogen distribution is the formation of a high core at the barmouth region during postmonsoon associated with waste discharged from sewage works and fishery industries on the northern region (Vypeen). The organic nature of the discharged waste and decay of dead organism often during late postmonsoon cause partial denitrification giving rise to high values of nitrite-nitrogen. The effluents discharged from the fertilizer factory situated on Periyar river bank and the leachate from the adjacent coconut husk retting grounds also contribute to the formation of the core of high values.

In the absence of large riverine sources, internally generated nitrites are spatially transported and distributed by the estuarine dynamics resulting in the sharp gradients on either sides of the barmouth. A significant monsoonal correlation between nitrite and salinity indicate that the distribution of estuarine nitrites are governed more by rate of freshwater influx. However, the correlation observed during postmonsoon may be the result of biological processes that control the distribution of nitrite rather than by the hydrodynamical features.

The distribution of nitrate-nitrogen and range of observed values are comparable with those reported by earlier workers. A core of high values of nitrate develops during monsoon in the vicinity of the barmouth. This feature can be interpreted by considering the influx of forestshed nitrate in freshwaters which contain abundant organic detritus matter; on oxidation, nitrates are liberated to the overlying waters. It is also suggested that the distribution of nitrates in this estuary is better regulated by biological processes during postmonsoon. Studies also indicated that nitrates behaved conservatively in this estuary during all seasons.

The studies on distribution of ammonia shows a clear seasonal dependance, viz monsoonal maximum and postmonsoonal minimum. The high values of ammonia in the northern regions is found to be associated with high values of nitrate-nitrogen. This observation is closely linked to the formation of nitrate via the ammonia-nitrite chain. It is likely that the previously sedimented organic matter decomposed by nitrifying bacteria increases the ammonia content during this period. However, the southern parts of the estuary do not contain any measurable amount of ammonia.

This study also accounts for the distribution and concentration of different forms of phosphorus. It was observed that inorganic reactive phosphorus (IRP) exhibits a seasonal variation on the northern parts: lower values being recorded during monsoon and higher values during postmonsoon and premonsoon. Adsorption of phosphorus from overlying waters by sedimenting particulates and dilution of estuarine waters by low phosphate bearing freshwaters can be attributed to low values observed during the monsoon. The high values of phosphorus observed during premonsoon in the northern region along with pronounced horizontal gradient both at surface and bottom can be interpreted as due to (i) the transport of industrial effluents with freshwater from Periyar river and from land drainage (ii) the loading and unloading of rock phosphate and fertilizers at Cochin barmouth and (iii) the desorption of phosphorus from sediments under favourable conditions. Comparatively, low phosphate values are observed on the southern parts with lesser seasonal variations.

Distribution of dissolved organic phosphorus (DOP) on the northern regions indicates lower values during monsoon due to biological utilization of DOP and its subsequent conversion of particulate phosphorus in this region. It is also suggested that DOP may be directly utilized when the inorganic phosphorus level becomes low enough to limit the algal growth. The low concentration of IRP and high values of particulate phosphorus (PRP) in the northern region during monsoon support the above view. The release of organic phosphorus from dead or dying organisms together with leaching of sediments give way to the observation of higher values of DOP during postmonsoon. The concentration of DOP gradually increases from the southern tip to the Cochin barmouth area. However, compared to the northern regions, the values indicate low inputs from river water or land drainage. A significant positive correlation was observed between salinity and DOP. However, wide scatter of the values during postmonsoon signify a transitory behaviour for DOP.

Particulate reactive phosphorus exhibits high values in the northern regions during monsoon, reflecting the fact that several simultaneous processes may be taking place such as (i) the conversion of DOP to PRP as a result of planktonic utilization of DOP when relative IRP concentrations are very low (ii) the transport of particulate matter by run off and (iii) turbulent mixing of bottom waters with surface waters at shallow depths resuspending the sedimented matter. This area covered with organically rich silty clay and clayey silt favours the above contention. In the southern regions, the values are very low because of comparatively lower influx of particulate matter and also that the bottom bed is covered by more sandy materials. No significant correlation is observed between salinity and PRP.

Total reactive phosphorus (TRP) concentrations show low values in the northern regions explained as (i) adsorption of IRP, a fraction of TRP, from the overlying waters by sediments and (ii) lack of contributory sources such as terrestrial run off. Another characteristic feature is the high values of TRP during premonsoon associated with high values of IRP and low values of DOP reflecting TRP concentration to be influenced by discharge of industrial effluents. Added to the above feature, a perfect linearity was observed between TRP and IRP.

The studies on size composition of the sediments in the Cochin estuary indicate markedly varying features. The seasonal variations at each station is minimal. The northern part of the estuary where the northern branch of Periyar river joins, is characterised by a sandy zone. The sediments along the middle portion of the northern region consists of relatively higher percentage of clay and silt fraction. The Cochin harbour area is predominantly covered with silty clay and rest of the estuary (Southern parts) by clayey sand. It is concluded that coarse sand has a reduced displacement rate while extensive transport of silt and clay from freshwater zone to seaward side occur resulting in high silt and clay content at the barmouth region.

Finally the investigation looks into the variation of interstitial and adsorbed phosphorus in the sediments. These parameters are observed to be closely related to the texture of the sediments. The high values of interstitial and adsorbed phosphorus recorded during monsoon in the middle of the northern part of the estuary are associated with high percentage of silt which have larger retention capacity for phosphorus. The low salinities and high DO values of overlying waters during this period may further enhance the adsorption processes. The hydrographic conditions during premonsoon favour the desorption of phosphorus from sediments to the overlying waters. This result in the lowering of the interstitial and adsorbed phosphorus content resulting in higher values of IRP in the northern region. The low values recorded in the southern regions are characterized by clayey sand with high amounts of sand content. The minute variations of pH values observed in overlying water during this investigation is not likely to influence the rate of exchange of phosphates between sediments and overlying waters.

The distribution pattern of inorganic reactive silicate-silicon (RSi) has revealed that (i) silicate shows a spatial decrease from very high concentration at the freshwater end to low values at the seaward side during all seasons in this estuary and (ii) a gradual seasonal decrease during the period of observation. These spatial variations and seasonal decrease reflect the fact that silicate influx into the estuary is largely depend on the external sources like freshwater discharge and land drainage. One possible explanation for the high values of silicate during monsoon is the discharge of large volumes of silt-laden freshwater into the estuary by rivers. The decrease of silicate contents as season advances to postmonsoon and premonsoon is associated with the gradual decrease of river water flow and enhanced biological utilization.

The removal of silicate by flocculation through increased electrolytic concentration during the mixing of river water with seawater may contribute to the lower values of silicate during premonsoon in the northern part of estuary. The transport of silicate rich freshwater across the boundaries of the estuary, abstaining most removal processes turn out to be a marked feature for the southern part of Cochin estuary during monsoon period. The agencies bring about loss of silicate within the estuary, however, remain pronounced during non-monsoonal months only. Regressional analysis between salinity and silicate during any season suggest that silicate behaves conservatively in this estuary.

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ANNEXURE 1

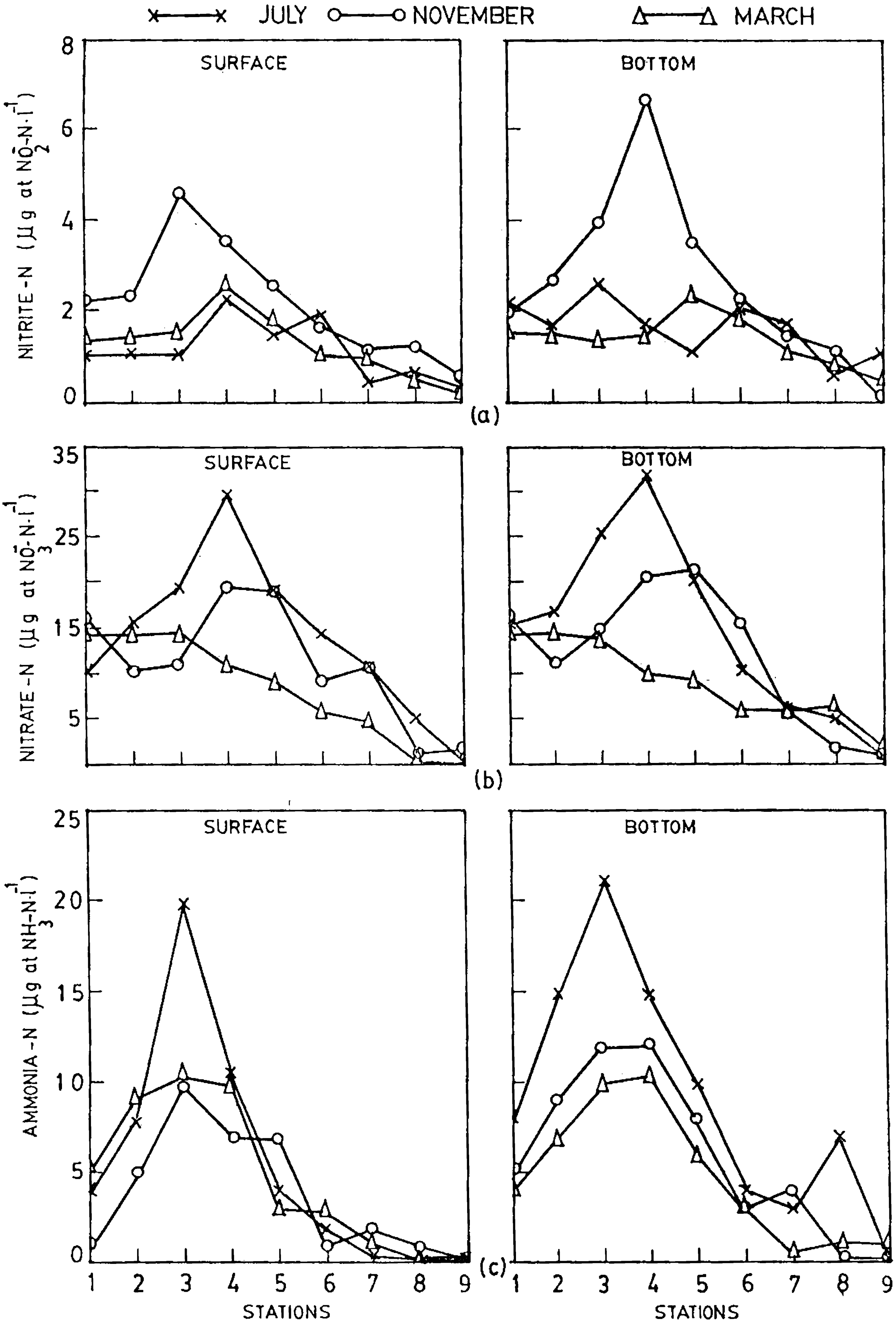

Fig. 24. Representative seasonal distribution of nitrite-nitrogen (a), nitrate - nitrogen (b) and ammonia - nitrogen (c) at stations 1 to 9.

ANNEXURE 2

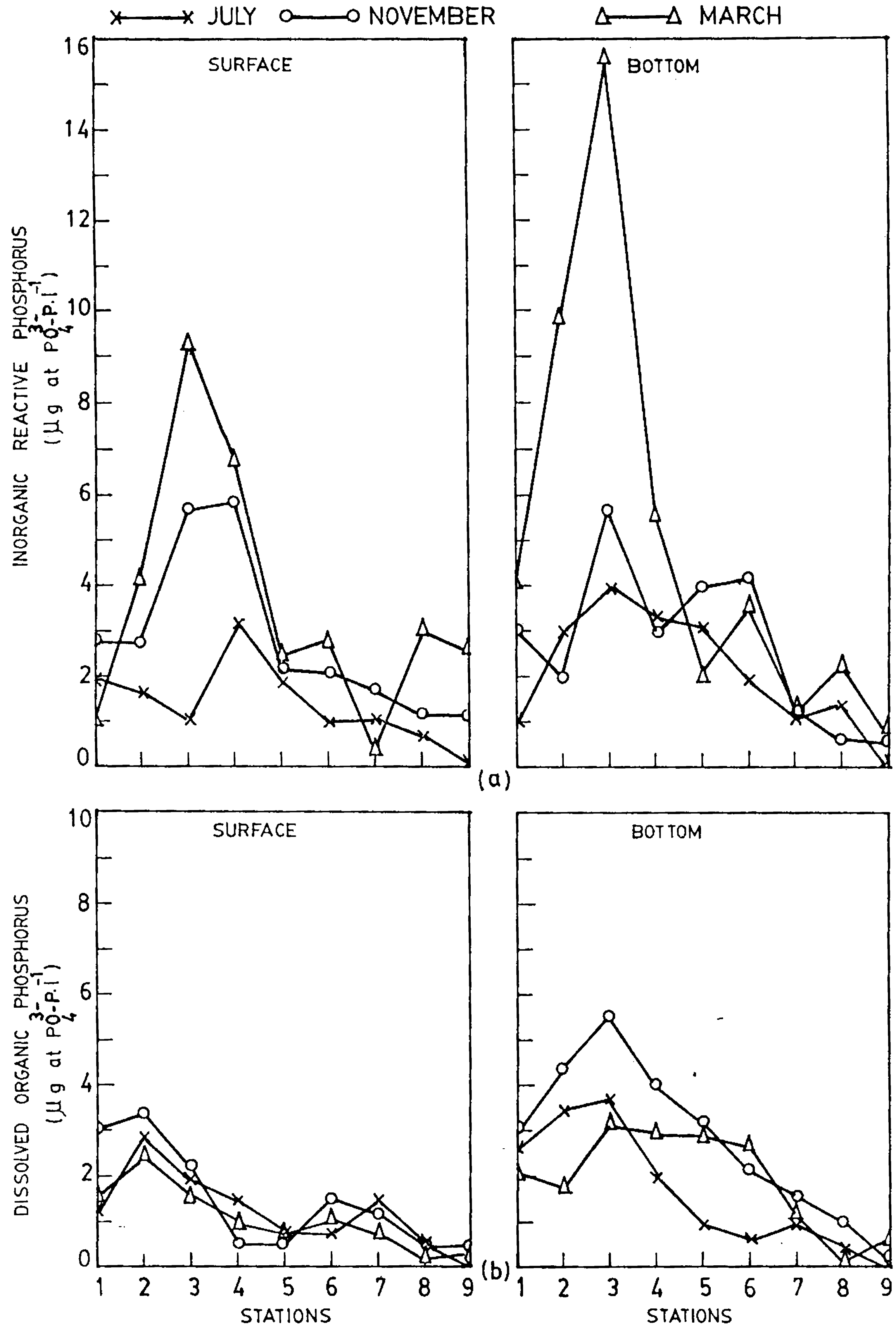

Fig. 25. Representative seasonal distribution of inorganic reactive phosphorus (a) and dissolved organic phosphorus (b) at stations 1 to 9.

ANNEXURE 3

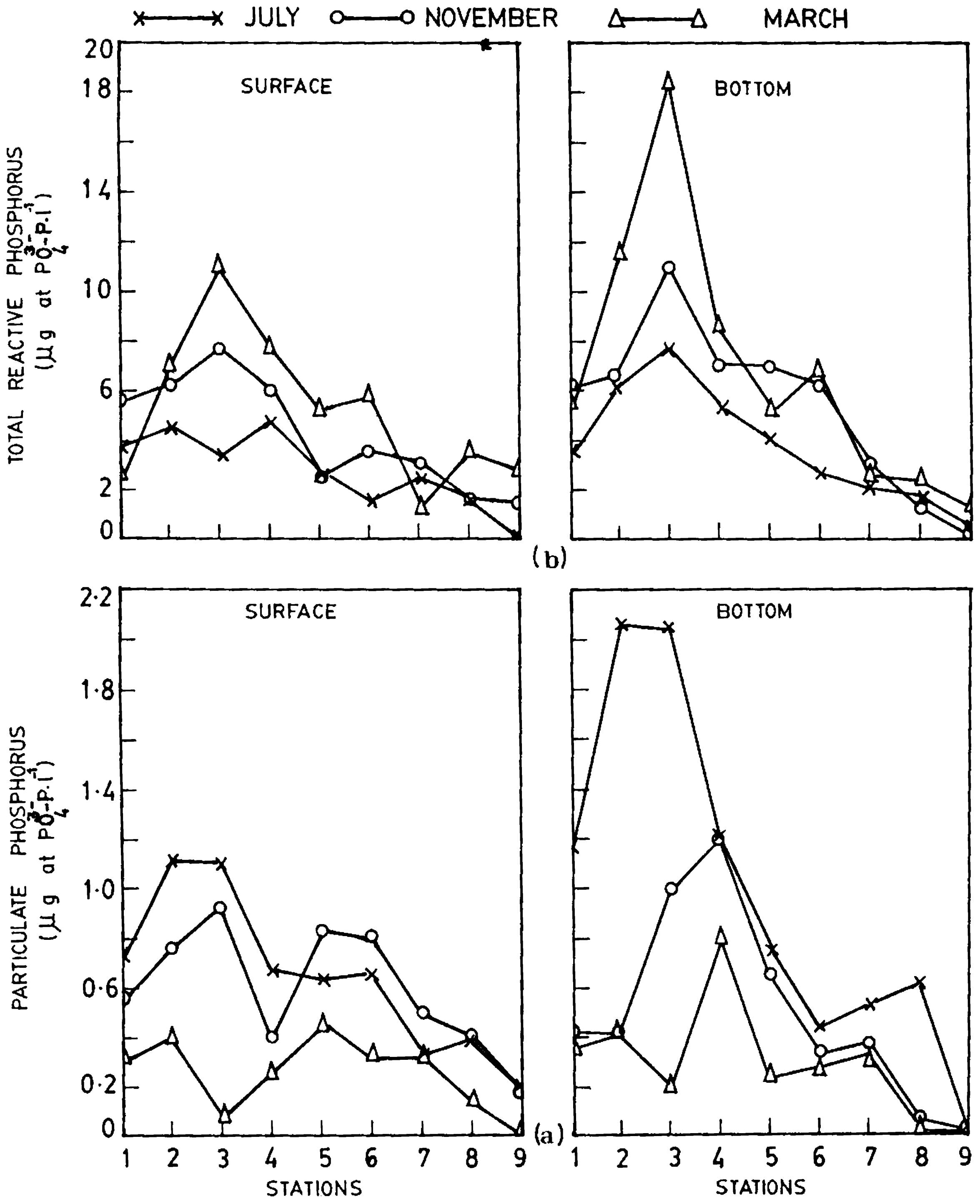

Fig. 26. Representative seasonal distribution of particulate reactive phosphorus (a) and total reactive phosphorus (b) at stations 1 to 9.

ANNEXURE 4

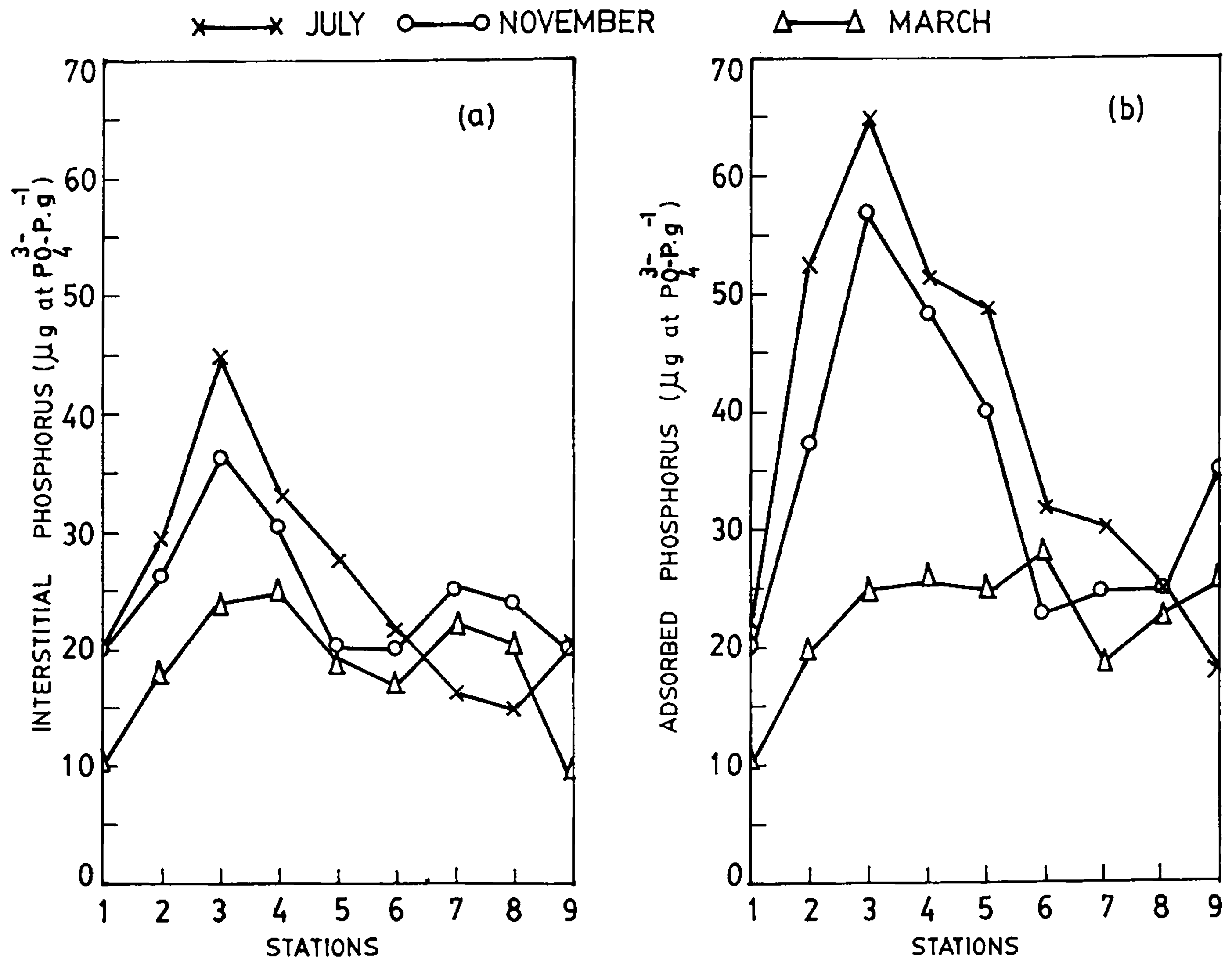

Fig. 27. Representative seasonal distribution of interstitial phosphorus (a) and adsorbed phosphorus (b) at stations 1 to 9.

ANNEXURE 5

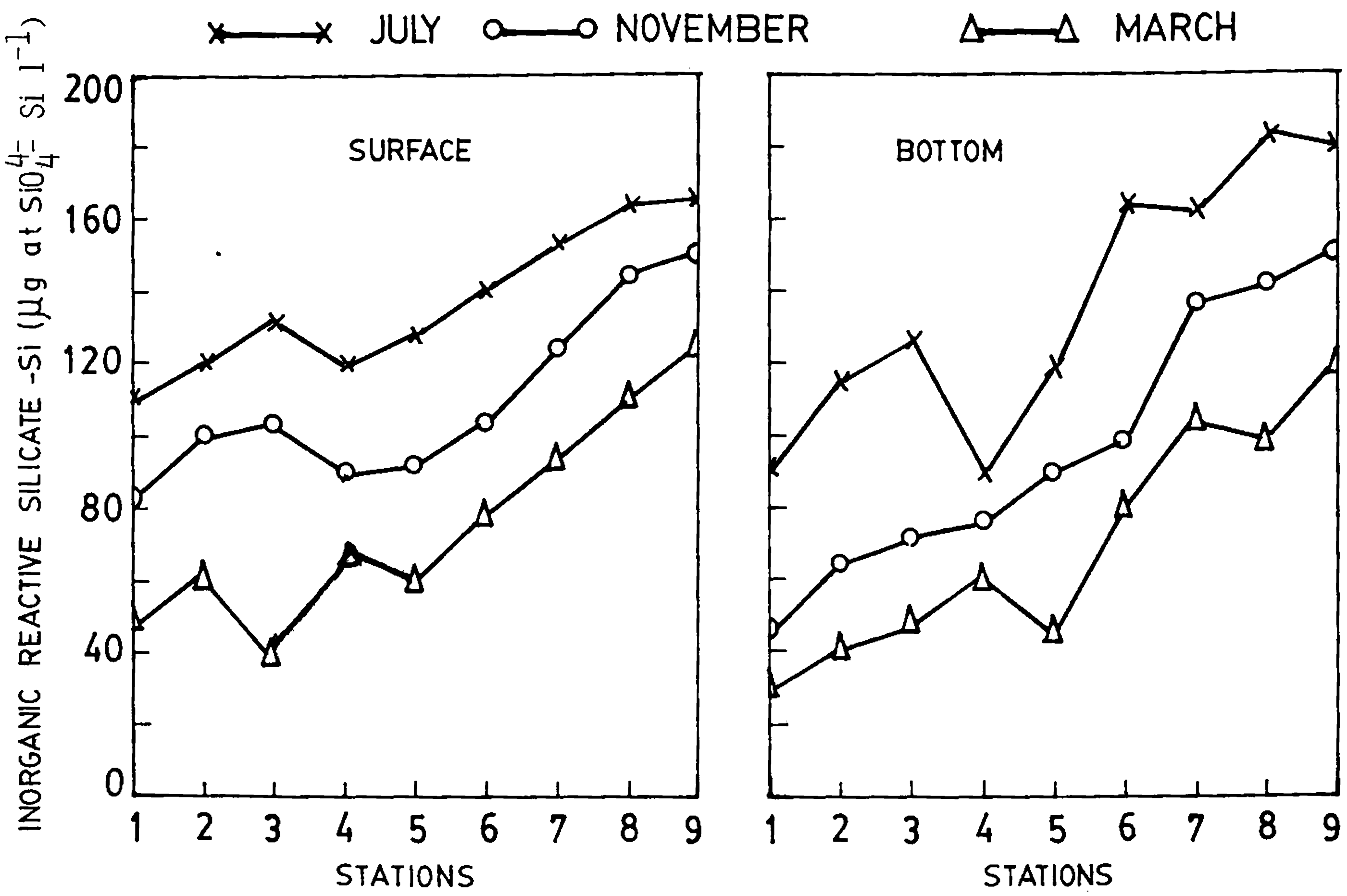

Fig. 28. Representative seasonal distribution of inorganic reactive silicate - silicon at stations 1 to 9.

Table 1. Distribution of temperature (°C) in the Cochin estuary during June 1985 to May 1986.

on	1		2		3		4		5		6		7		8		9	
h	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
	28.5	27.9	28.6	28.3	28.1	27.9	28.0	30.3	28.3	29.1	27.4	28.0	27.1	27.0	27.0	27.0	27.7	26.3
	28.0	26.1	27.1	28.1	27.6	27.4	27.7	30.1	28.1	28.0	27.6	27.1	27.6	27.9	28.1	27.6	27.6	26.1
	28.0	27.3	26.7	27.4	26.8	26.8	28.1	29.0	27.9	28.1	26.6	27.3	26.3	27.1	27.5	26.5	27.1	27.8
	27.6	27.2	27.3	26.1	26.1	25.3	27.3	28.1	27.1	27.0	26.3	26.1	26.1	26.0	27.1	26.9	27.1	26.1
	27.8	27.4	27.4	25.3	25.3	26.2	26.1	26.7	28.8	27.6	26.8	26.2	25.3	26.1	27.3	25.8	27.1	26.1
	28.1	27.8	27.3	26.3	27.3	27.3	26.3	26.3	27.3	27.6	26.7	26.3	26.3	26.1	26.1	25.6	27.4	25.6
	28.3	28.0	28.1	28.1	28.6	28.1	27.3	26.2	28.1	28.3	27.7	27.1	27.6	26.0	26.1	26.1	27.6	26.1
	28.4	27.8	28.3	27.9	28.3	28.1	26.9	27.6	28.4	28.6	28.3	27.6	27.7	27.3	26.1	26.2	27.3	25.1
	28.7	28.3	27.6	27.6	27.9	27.6	28.4	27.1	28.0	28.1	28.0	28.3	27.9	28.1	27.3	26.3	27.9	25.3
	29.3	28.4	27.1	28.1	28.7	28.1	28.7	28.3	29.1	28.1	29.1	29,.1	28.1	27.6	27.6	27.1	26.8	26.6
	30.1	27.1	29.1	28.8	30.1	27.1	29.3	29.1	30.3	29.3	28.6	28.1	27.7	28.1	28.1	26.9	26.4	27.4
	30.7	28.3	29.3	29.1	30.1	28.3	30.4	29.6	30.1	29.1	29.6	28.6	28.6	28.1	28.1	28.1	27.5	29.3
	31.1	29.4	30.6	28.7	30.1	28.6	31.1	30.1	30.0	29.4	30.4	29.0	29.1	29.0	29.1	28.3	28.6	28.1
	31.0	29.7	31.7	29.1	31.6	29.1	31.3	30.7	31.1	29.9	29.7	29.1	30.6	28.1	29.1	28.6	27.9	27.6
	32.3	30.1	32.3	29.3	32.1	30.3	32.3	31.4	31.1	30.1	30.1	28.7	29.7	29.1	29.4	29.1	27.8	28.3
	32.1	31.1	33.0	30.0	32.4	30.6	32.6	31.4	32.0	29.8	29.1	30.1	30.6	30.1	28.7	29.1	29.0	28.0
	31.9	30.7	32.1	31.4	32.0	31.9	32.3	30.6	32.3	29.7	30.1	30.1	30.7	30.0	29.2	29.0	28.7	28.1
	33.1	32.1	32.3	31.4	33.4	32.6	32.7	31.7	31.9	30.6	30.1	30.3	29.8	29.1	30.1	29.2	29.1	28.3
	33.0	31.8	32.6	31.4	32.1	31.7	33.0	30.8	32.7	30.1	30.1	30.1	29.1	29.3	29.1	30.1	29.3	29.0
	32.2	31.7	31.9	31.3	32.1	32.0	32.7	32.1	31.7	31.2	29.3	30.1	30.7	29.2	29.2	29.0	28.7	29.0
	32.0	31.9	33.1	30.6	31.8	31.6	32.0	31.8	30.8	30.9	29.0	29.1	29.3	29.1	29.0	29.3	29.1	29.0

S - Surface, B - Bottom

Table 2. Distribution of salinity ($x10^{-3}$) in the Cochin estuary during June 1985 to May 1986.

1		2		3		4		5		6		7		8		9	
S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
8.08	20.11	07.56	16.16	12.16	16.31	11.86	19.00	05.16	12.06	02.41	04.30	01.01	01.81	00.00	00.00	00.00	00.00
8.16	21.39	07.03	14.81	11.40	15.46	10.36	18.20	06.37	11.16	03.06	04.18	02.10	01.10	00.00	00.00	00.00	00.00
9.23	20.48	07.34	16.78	11.06	18.38	09.21	19.00	07.58	15.00	03.91	06.71	01.95	01.10	00.50	00.00	00.00	00.00
9.46	21.67	07.68	15.36	07.78	17.38	07.42	19.30	07.91	13.10	05.97	09.99	01.41	03.06	00.36	00.46	00.36	00.16
1.23	23.87	09.10	16.46	07.00	19.61	10.23	20.00	09.10	15.60	07.51	08.07	02.06	02.86	00.41	00.76	00.80	00.96
3.87	20.96	11.00	19.01	08.06	19.10	10.16	27.10	11.12	17.20	09.56	11.07	02.71	05.50	00.20	02.61	00.71	02.01
5.61	26.11	12.36	19.31	09.10	20.20	10.61	28.81	10.14	19.20	10.41	12.06	03.10	07.76	00.10	03.13	00.08	03.06
15.18	25.23	10.46	16.63	11.20	21.46	13.61	28.81	10.34	19.50	10.46	14.01	02.16	06.68	00.96	02.41	00.60	04.31
16.30	20.41	13.81	18,93	14.30	23.63	16.01	29.81	14.35	22.81	11.33	14.22	07.86	08.70	01.06	04.56	00.76	05.62
17.61	27.71	15.56	19.31	15.61	24.81	19.62	29.00	15.68	23.46	12.10	15.11	04.01	07.32	03.76	06.61	01.06	07.94
19.57	29.61	14.54	21.41	18.81	23.76	20.44	32.18	17.10	26.31	14.10	19.66	06.81	10.10	01.08	07.18	01.86	08.14
20.35	30.51	18.30	19.31	16.30	24.86	20.21	30.60	19.90	25.60	10.01	16.50	09.11	11.10	04.08	06.23	00.96	06.96
23.50	31.46	19.46	21.61	20.10	27.11	23.32	32.60	20.12	27.70	13.01	17.05	08.61	10.86	02.14	09.46	03.61	07.31
20.61	30.21	21.51	21.26	18.16	29.20	25.16	30.90	22.22	27.80	12.00	18.00	10.30	12.10	03.40	11.55	04.10	08.18
24.00	32.16	23.68	25.31	19.36	31.30	27.82	30.30	23.21	29.71	16.00	19.00	11.41	11.35	06.67	11.56	03.30	07.81
31.36	31.87	20.34	23.61	22.00	29.41	31.61	35.46	19.14	28.80	16.66	20.30	10.60	13.68	09.99	10.35	05.30	10.86
33.84	30.98	26.26	27.81	24.00	27.50	32.32	34.20	25.25	30.10	19.11	19.60	09.54	13.11	11.06	14.40	06.34	12.12
35.02	35.21	37.54	28.36	24.60	30.60	30.61	35.16	27.17	31.61	19.30	23.83	11.37	15.34	11.81	13.81	07.87	10.21
32.13	34.03	29.36	31.32	31.30	34.31	35.06	30.30	29.29	30.31	20.29	23.91	15.06	15.16	13.40	15.01	06.98	09.32
34.16	35.00	32.30	35.01	30.60	33.31	31.01	31.18	30.10	29.01	21.18	21.11	15.61	13.26	12.84	15.96	08.61	11.81
33.80	34.50	31.86	34.50	31.00	30.61	30.61	33.10	31.00	27.80	20.56	20.50	14.06	10.86	11.10	16.06	11.50	10.80

S - Surface, B - Bottom

Table 3. Distribution of pH in the Cochin estuary during June 1985 to May 1986.

1		2		3		4		5		6		7		8		9	
S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
7.40	7.75	7.30	8.05	7.40	8.15	7.20	8.15	7.00	7.05	7.15	7.05	7.20	7.25	6.95	6.85	6.60	6.80
7.50	7.50	7.05	8.15	7.10	8.20	7.00	8.20	7.30	7.10	7.30	7.20	7.35	7.10	6.90	6.70	6.80	6.70
7.80	7.40	7.25	7.80	7.20	8.00	7.45	8.20	7.20	7.25	7.20	7.15	7.00	7.25	6.85	6.95	7.05	6.80
7.95	7.60	7.40	7.50	7.00	7.80	7.40	8.20	7.15	7.05	7.20	7.15	7.20	7.30	6.60	7.10	6.95	6.80
7.90	7.80	7.50	7.45	7.15	7.60	7.05	8.05	7.45	7.05	7.20	7.10	7.40	7.05	6.70	7.00	7.25	7.10
7.70	8.20	7.85	7.80	7.55	7.45	7.30	7.45	7.00	7.20	7.40	7.20	7.00	7.35	6.60	7.30	7.30	6.40
8.00	8.10	7.90	7.60	7.50	7.85	7.75	7.80	7.45	7.45	7.50	7.20	7.05	7.25	6.85	7.35	6.85	6.80
8.15	8.00	7.75	7.50	7.60	7.85	7.85	7.90	7.85	7.80	7.85	7.74	7.15	7.30	7.10	7.40	6.60	7.00
8.20	7.90	8.15	7.50	7.85	7.70	8.05	8.00	7.95	7.85	7.60	7.45	7.25	7.20	7.05	7.30	6.60	7.10
8.05	7.90	8.10	7.70	8.20	7.60	8.20	8.15	8.20	7.85	7.40	7.30	7.25	7.40	7.10	7.45	6.85	7.30
7.70	7.80	7.80	7.50	7.85	7.60	7.90	8.00	8.10	8.05	7.65	7.20	7.05	7.40	7.30	7.30	7.30	7.40
7.60	8.20	7.75	7.45	8.00	7.50	8.10	8.00	8.05	8.00	7.75	7.45	7.05	7.40	7.35	7.40	7.20	7.40
7.55	7.95	7.60	7.50	7.90	7.40	8.15	7.80	8.15	8.05	7.75	7.10	7.05	7.50	7.40	7.40	7.10	7.05
7.60	7.95	7.80	7.60	8.15	7.75	7.60	7.40	7.95	7.80	7.80	7.05	7.05	7.40	7.30	7.25	7.25	7.30
7.70	7.85	7.90	7.45	8.05	7.80	7.75	7.50	7.80	7.45	7.35	7.25	7.15	7.20	7.25	7.05	7.20	7.45
7.85	7.65	8.00	7.75	7.75	7.55	7.55	7.50	7.60	7.40	7.00	6.35	7.15	7.00	7.00	7.00	7.15	7.30
7.90	7.55	7.75	7.65	7.85	7.70	7.45	7.40	7.40	7.25	7.05	7.05	7.05	7.10	7.20	7.00	7.00	7.00
8.15	7.70	7.60	7.45	7.50	7.45	7.50	7.70	7.50	7.25	7.15	6.00	7.25	7.45	7.35	7.10	7.20	7.05
7.75	7.40	7.50	7.70	7.60	7.65	7.85	7.60	7.45	7.15	7.05	6.30	7.25	7.35	7.00	7.40	7.10	7.05
8.25	7.40	7.80	7.80	7.40	7.30	7.70	7.80	7.40	7.00	7.10	6.60	7.05	7.25	7.15	7.35	7.00	7.40
8.05	7.50	7.55	7.40	7.70	7.50	7.55	7.60	7.50	7.00	7.10	7.00	7.10	7.40	7.25	7.05	7.25	7.15

S - Surface, B - Bottom

Table 4. Distribution of dissolved oxygen (ml l^{-1}) in the Cochin estuary during June 1985 to May 1986.

Station	1		2		3		4		5		6		7		8		9	
Month	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
Jun.	5.86	4.90	5.50	5.06	5.10	5.37	6.45	5.06	6.57	6.01	7.70	7.71	8.07	6.53	7.50	6.30	7.71	6.56
1985	5.30	5.36	4.75	4.91	5.56	5.61	6.14	5.31	6.50	5.31	7.91	7.01	7.96	7.01	7.70	6.40	7.78	6.57
Jul.	6.09	5.06	5.13	5.30	5.63	5.56	5.90	5.61	6.36	6.01	7.43	7.67	7.61	7.50	7.13	6.50	7.33	6.90
	6.27	4.71	4.96	5.07	5.76	5.07	6.00	5.10	6.10	6.11	7.30	6.60	8.13	7.17	7.91	7.06	7.99	6.90
Aug.	6.37	5.56	5.56	5.51	6.04	5.37	6.13	5.17	5.71	6.61	7.14	6.51	8.34	7.86	8.06	7.06	7.68	6.76
Sept.	6.05	5.86	6.04	5.13	6.31	5.06	6.37	5.60	6.31	6.17	7.07	6.67	7.95	7.57	8.50	8.00	8.07	7.00
	6.17	5.17	6.51	5.06	6.47	5.16	6.26	5.37	6.78	6.31	7.57	6.10	8.06	7.46	8.40	8.31	8.31	7.00
Oct.	5.87	6.07	6.46	4.97	6.56	5.10	6.46	5.51	6.53	6.26	7.80	6.10	8.02	7.06	8.57	7.50	8.21	7.58
	6.09	5.71	6.15	4.26	6.36	5.50	6.26	5.46	6.76	6.30	7.34	5.90	8.31	7.36	8.57	8.50	7.97	7.63
Nov.	5.91	5.51	6.50	5.57	6.81	5.36	6.00	5.53	6.14	6.17	7.20	6.21	8.06	6.50	8.50	7.10	8.56	7.16
Dec.	6.34	6.34	6.07	5.60	6.07	5.01	6.31	5.61	6.15	5.50	6.13	7.00	7.50	6.20	8.06	7.00	8.14	7.00
	6.34	5.70	5.81	5.06	6.56	5.41	6.10	5.07	5.90	5.70	7.00	7.07	7.96	6.38	7.93	6.09	8.53	7.00
Jan.	6.06	5.13	5.90	5.13	6.07	5.41	6.20	4.90	6.73	5.86	7.13	6.01	7.38	7.10	7.31	6.50	8.30	7.03
	5.91	4.91	6.36	4.54	6.13	5.00	6.13	4.70	6.07	5.13	6.98	6.71	7.70	6.00	7.56	6.30	8.06	7.03
Feb.	5.74	4.54	6.07	4.71	6.07	4.50	6.03	4.56	5.97	5.31	6.98	5.20	7.66	6.00	7.07	7.60	7.56	7.10
Mar.	5.94	4.44	5.93	4.06	5.56	4.06	6.13	4.30	6.30	5.44	7.10	5.53	7.57	6.62	7.01	5.71	7.57	6.50
	5.84	4.10	5.51	3.50	5.10	4.86	5.90	4.26	6.00	5.41	7.00	5.51	7.61	5.34	6.01	6.10	7.31	6.50
Apr.	5.51	4.30	5.46	3.31	5.06	3.56	5.10	4.01	5.90	5.30	7.16	5.31	7.16	5.53	6.90	6.10	7.40	6.51
	5.16	4.16	5.00	3.23	4.57	3.07	5.56	4.34	5.73	5.60	6.57	5.77	7.03	6.06	7.73	6.10	7.03	7.00
May	5.60	4.06	5.14	3.46	4.06	3.08	5.01	3.56	5.00	5.40	6.31	5.77	7.06	5.96	7.06	6.23	7.61	7.00
1986	5.34	4.60	5.21	3.46	4.34	3.39	5.70	3.91	5.41	5.60	6.10	5.57	6.80	6.16	7.11	6.41	7.61	6.51

S - Surface, B - Bottom

NITROGENOUS NUTRIENTS IN SOME KERALA ESTUARIES

Table 5. Seasonal and annual averages of nitrogenous nutrients for the water column. (Values are in µg at l^{-1} and ranges are given in parenthesis). Sarala Devi *et al*. (1983)

Season	Nitrite	Nitrate	Ammonia
	KALLAI		
Premonsoon	0.58 (0.10-1.77)	0.61 (0-02.54)	13.90 (04.36-28.55)
Monsoon	1.16 (0 - 2.64)	14.23 (0-43.46)	15.70 (11.52-20.29)
Postmonsoon	0.63 (0.33-0.73)	0.27 (0-0.53)	7.24 (5.44-9.04)
Annual	0.80 (0 - 2.64)	5.42 (0-43.46)	13.54 (4.36-28.55)
	BEYPORE		
Premonsoon	0.53 (0.2-1.64)	2.88 (0.58-9.12)	5.97 (0.88-13.77)
Monsoon	0.05 (0 - 0.3)	11.26 (13.6-19.04)	11.31 (2.88-46.02)
Postmonsoon	2.16 (0 - 6.13)	4.54 (0.59-7.19)	3.30 (2.58-3.87)
Annual	0.67 (0 - 6.13)	6.23 (0-19.04)	7.61 (0.88-46.02)
	KORAPUZHA		
Premonsoon	0.59 (0-2.45)	1.60 (0.29-3.68)	4.80 (1.77-7.27)
Monsoon	0.10 (0-0.43)	6.23 (0.63-10.75)	4.18 (2.21-7.44)
Postmonsoon	1.15 (0.42-2.81)	1.43 (0 - 2.43)	12.40 (2.83-33.57)
Annual	0.61 (0-2.81)	4.31 0 - 10.75)	5.50 (1.77-33.57)
	MAHE		
Premonsoon	0.80 (0.11-2.82)	2.87 (0 - 7.34)	7.10 (0-24.64)
Monsoon	0.04 (0-0.11)	10.04 (0.4-18.09)	12.47 (1.68-60.89)
Postmonsoon	0.65 (0.42-1.04)	0.66 (0 - 1.06)	2.96 (1.52-7.75)
Annual	0.50 (0 - 2.82)	5.20 (0 - 18.09)	8.58 (0 -60.89)

Table 6. Concentrations of nitrite - nitrogen (µg at NO_2^--N l^{-1})in the Cochin estuary during June 1985 to May 1986.

Station	1		2		3		4		5		6		7		8		9	
Month	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
Jun.	1.47	2.00	1.63	1.76	1.48	1.73	1.43	2.61	1.27	2.31	1.30	1.69	0.27	1.36	0.16	0.47	0.08	0.23
1985	1.61	1.70	1.68	1.95	1.52	1.68	1.28	2.61	0.95	1.97	1.18	1.93	0.32	1.38	0.13	0.63	0.13	0.32
Jul.	2.21	2.43	1.83	1.48	1.80	2.43	2.56	2.00	1.30	1.95	2.03	1.68	0.43	1.28	0.06	0.38	0.23	0.58
	1.08	2.13	1.07	1.66	1.10	2.63	2.33	1.73	1.50	1.63	1.87	2.08	0.43	1.68	0.63	0.56	0.43	1.01
Aug.	1.93	2.45	1.57	1.94	1.51	3.51	1.56	2.43	2.45	2.06	2.01	2.18	0.57	2.03	0.87	0.36	0.37	0.90
Sep.	2.15	2.38	2.06	2.41	2.40	3.90	1.74	3.56	1.78	2.47	1.63	2.31	1.03	1.43	0.93	0.96	0.23	0.78
	2.40	2.17	1.71	2.54	1.57	4.02	1.56	4.67	1.90	2.47	1.87	2.03	1.14	1.68	1.38	1.40	0.43	0.23
Oct.	2.76	1.68	2.13	2.48	3.59	4.13	2.37	5.58	2.45	2.56	1.45	2.47	1.27	0.98	1.36	1.46	0.16	0.78
	2.36	1.63	2.25	2.78	3.36	3.88	2.81	5.97	2.06	2.90	1.47	2.41	1.43	1.87	0.96	1.42	0.10	0.40
Nov.	2.17	1.98	2.41	2.68	4.57	4.00	3.59	6.68	2.63	3.50	1.67	2.13	1.06	1.57	1.16	0.93	0.62	0.16
Dec.	1.68	1.63	2.56	2.47	4.75	4.18	5.58	6.35	3.40	3.58	1.90	1.68	1.93	1.68	0.83	1.90	0.66	0.26
	2.03	3.56	2.40	2.68	3.96	3.56	3.57	5.86	3.03	3.78	1.80	1.73	1.22	1.38	0.63	0.87	0.70	0.49
Jan.	2.15	1.78	2.68	2.68	3.18	2.56	5.28	4.50	3.45	3.06	1.71	1.48	1.22	1.33	0.37	1.07	0.38	0.32
	2.01	1.45	2.00	2.68	3.00	2.07	4.50	3.57	2.47	3.40	1.40	1.53	1.30	1.43	0.48	0.30	0.10	0.18
Feb.	1.38	1.13	1.75	2.51	2.40	2.41	3.58	3.86	2.58	2.51	1.30	1.53	1.33	1.50	0.96	0.63	0.31	0.51
Mar.	1.57	1.40	1.87	1.90	2.14	1.93	3.06	2.48	2.01	2.61	1.68	0.96	1.17	1.37	0.47	0.47	0.27	0.38
	1.30	1.56	1.37	1.58	1.36	1.43	2.46	1.51	1.57	2.40	0.96	1.88	0.96	1.11	0.63	0.87	0.23	0.37
Apr.	1.20	1.56	1.01	0.90	0.86	1.91	1.51	0.96	0.90	2.56	0.78	1.48	0.86	0.57	0.84	0.58	0.21	0.32
	0.90	0.96	0.86	0.63	0.77	1.59	0.85	0.75	0.70	1.46	0.55	1.37	1.11	0.43	0.55	0.30	0.23	0.38
May	1.10	1.51	0.97	0.78	1.43	1.59	0.90	0.68	0.64	0.75	0.63	1.58	0.47	0.32	0.32	0.58	0.21	0.30
1986	0.90	1.15	0.86	0.67	0.86	0.90	0.75	0.68	0.83	0.60	0.59	1.38	0.38	0.30	0.17	0.37	0.27	0.30

S - Surface, B - Bottom

Table 7. Concentrations of nitrate - nitrogen (µg at NO_3^--N l^{-1}) in the Cochin estuary during June 1985 to May 1986.

1		2		3		4		5		6		7		8		9	
S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
08.76	15.68	16.43	18.36	24.60	25.70	23.70	22.00	16.35	21.86	10.06	11.72	09.90	08.16	03.10	02.86	02.38	00.94
09.00	14.38	17.16	19.34	21.91	26.81	25.86	27.60	15.38	20.44	11.32	12.61	10.34	09.26	04.94	03.41	01.24	00.80
10.13	13.46	18.38	20.67	22.31	25.92	24.33	30.55	19.70	24.10	12.20	14.34	09.87	09.36	04.53	05.53	00.74	00.89
10.16	15.49	15.56	16.57	19.36	26.30	28.94	34.44	19.40	21.27	14.30	10.76	11.70	07.33	05.36	06.26	00.96	02.01
12.51	15.57	16.35	18.32	18.87	24.90	30.95	38.95	18.36	22.61	10.10	14.56	10.80	06.40	06.61	04.33	01.97	00.98
13.00	16.32	14.80	16.86	14.70	20.81	22.68	38.31	19.61	20.31	09.90	11.51	12.12	10.76	04.68	03.64	01.34	03.46
15.81	16.44	14.36	14.32	16.30	16.71	20.90	34.61	18.81	25.41	10.81	13.46	10.36	08.66	05.47	03.00	02.68	03.86
14.56	15.61	13.80	14.46	15.52	15.91	20.15	26.48	17.20	22.31	08.61	16.41	10.70	06.13	04.16	03.41	01.34	01.38
15.30	14.61	11.30	13,07	14.30	15.31	19.91	19.30	16.14	20.54	06.66	13.81	10.82	06.13	04.23	03.86	04.67	01.60
16.90	16.34	09.55	12.42	12.28	14.70	18.71	20.56	18.32	21.61	07.70	15.61	11.50	06.13	02.34	02.71	02.67	01.57
10.36	14.08	10.96	10.66	11.97	13.60	17.67	18.15	14.60	18.70	04.70	14.76	11.11	06.10	02.95	02.60	03.41	00.98
12.94	13.91	09.88	11.98	10.90	14.35	14.40	17.71	13.40	17.86	05.83	10.91	08.38	06.70	02.83	02.40	01.06	01.44
10.80	14.72	09.76	10.71	08.71	13.87	13.68	16.80	11.34	14.60	06.30	11.81	07.20	07.01	02.56	02.31	01.10	01.32
10.30	14.06	09.30	12.35	09.60	12.61	14.00	14.60	10.86	15.15	05.50	12.46	08.81	07.01	03.68	03.86	00.86	00.98
13.32	13.36	12.55	11.51	11.34	10.81	11.86	12.16	10.32	10.61	05.81	10.38	08.91	08.06	02.10	03.34	02.00	00.80
12.78	10.13	12.46	12.17	12.62	13,37	10.90	10.16	13.60	09.91	06.00	08.56	06.70	07.31	01.80	05.96	01.10	00.80
14.18	14.13	14.32	13.60	13.81	14.06	11.57	09.87	09.40	08.81	07.00	07.40	04.58	06.91	00.30	06.10	00.91	02.10
10.44	10.11	11.11	14.70	11.11	10.00	09.90	14.30	10.63	06.66	06.76	06.31	02.31	03.41	01.10	03.85	00.67	03.01
06.00	08,60	09.06	12.86	07.39	09.17	13.73	10.40	11.32	05.90	02.34	06.36	01.06	02.56	01.41	02.10	00.20	02.00
05.38	06.81	06.98	09.96	06.50	07.60	10.93	08.96	10.70	06.66	01.81	03.30	00.19	03.00	01.80	01.96	00.96	02.10
03.10	04.68	04.13	08.81	04.10	06.71	08.15	07.56	09.08	06.60	00.96	05.16	00.16	02.31	00.90	02.31	00.86	02.10

S - Surface, B - Bottom

Table 8. Concentrations of ammonia - nitrogen (μg at NH_3-N l^{-1}) in the Cochin estuary during June 1985 to May 1986.

1		2		3		4		5		6		7		8		9	
S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
05.68	07.86	11.81	16.86	16.98	18.60	12.10	10.82	03.81	07.46	03.01	03.86	02.85	01.90	00.05	01.96	00.05	01.76
04.51	09.07	10.63	13.21	18.32	21.90	10.00	14.46	06.01	08.31	03.01	06.01	00.76	02.31	00.06	00.46	00.08	00.86
05.48	08.08	07.86	14.10	18.16	24.46	07.60	14.40	06.76	09.97	02.61	03.06	00.86	03.06	00.05	02.31	00.08	00.10
03.90	08.11	08.36	15.01	20.16	21.31	10.81	15.01	04.00	10.01	02.01	04.00	00.10	03.36	00.05	06.56	00.06	00.34
02.81	08.63	09.67	13.96	21.10	24.01	11.10	10.86	07.68	12.06	03.61	03.09	00.46	04.68	00.91	02.61	00.05	00.28
02.96	07.87	04.78	13.96	18.06	21.01	12.10	10.86	04.80	12.16	01.67	04.87	00.31	05.96	00.30	00.86	00.05	00.70
02.35	06.43	07.11	14.08	14.68	18.32	09.51	10.30	05.05	11.47	02.32	03.47	01.26	02.90	00.10	01.16	00.05	00.18
03.46	06.55	08.07	11.67	10.41	15.87	08.80	13.60	06.00	12.01	00.96	04.06	01.26	01.10	01.30	03.00	00.10	00.06
02.38	04.66	08.07	09.31	10.01	11.81	06.86	10.71	07.32	09.37	01.18	02.01	00.86	02.30	01.10	02.06	00.10	00.07
01.08	04.77	05.10	08.71	09.93	12.11	06.76	12.11	06.81	08.06	01.06	03.00	02.31	03.60	01.00	00.16	00.20	00.05
00.86	05.41	03.08	02.01	06.11	11.00	03.11	10.97	04.61	07.69	00.63	03.70	00.82	01.47	00.50	00.86	00.09	00.06
03.16	03.66	02.76	09.81	09.91	10.30	03.65	11.06	06.01	07.81	02.36	01.91	01.10	00.87	00.70	02.00	01.00	00.05
02.38	08.31	03.46	06.07	06.95	09.82	02.85	10.06	04.28	06.01	01.96	01.01	01.10	01.08	00.30	01.86	00.90	00.05
04.08	06.08	03.80	04.56	08.20	09.62	06.06	09.81	02.57	07.30	00.87	01.01	00.30	01.57	00.40	00.96	00.30	00.86
05.46	04.41	06.67	08.71	10.10	09.47	08.30	10.41	03.18	06.60	01.11	02.06	00.81	01.87	01.00	01.11	00.05	00.18
06.06	02.86	09.00	07.98	11.00	12.54	08.25	10.50	03.18	06.01	02.76	03.96	01.26	00.91	00.05	00.96	00.05	00.10
05.18	03.87	09.16	06.91	09.87	09.56	10.11	10.41	03.68	05.96	02.61	02.87	00.90	00.62	00.07	00.96	00.06	01.08
05.40	04.46	10.96	09.70	08.94	10.05	07.41	09.85	05.61	04.44	01.63	03.41	00.46	00.38	00.09	01.71	00.08	00.96
06.36	05.31	11.00	10.06	06.36	11.00	09.34	11.30	04.30	03.33	03.01	02.10	01.28	00.16	00.20	00.06	00.08	00.08
06.16	07.06	10.00	09.87	04.85	10.06	10.60	12.06	07.38	03.83	02.86	01.06	00.36	00.80	00.06	00.07	00.05	00.09
05.84	07.86	08.75	10.45	05.85	09.85	09.10	08.08	05.81	04.44	04.01	00.91	00.06	00.07	00.05	00.05	00.05	00.07

S - Surface, B - Bottom

Table 9. Concentration levels of Phosphorus (µg at P l^{-1}) in some water systems

Water system	concentration (ug at P l^{-1})	Reference
Agricultural drainage	1.6 - 32.0	Snoeyink & Jenkins, 1980.
Lake surface water	0.3 - 1.3	
(Domestic waste water)		Stumm & Morgan, 1970.
Orthophosphate	160.0	
Triphosphate	97.0	
Pyrophosphate	32.0	
Organic phosphate	32.0	
(Estuarine system)		
Tamar estuary - England	0.0 - 1.3	Morris et al., 1981.
Delaware estuary - USA	0.05 - 5.0	Sharp et al., 1982.
Mandovi-Zuari-India	1.3 - 7.5	Qasim & Sen Gupta, 1981.

Table 10. Concentrations of inorganic reactive phosphorus (µg at PO_4^{3-}-P l^{-1}) in the Cochin estuary during June 1985 to May 1986.

Station	1		2		3		4		5		6		7		8		9	
Month	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
Jun.	01.23	04.07	00.43	04.90	00.57	03.11	01.63	03.81	02.41	03.80	01.07	01.76	00.82	01.10	00.47	00.86	00.00	00.18
1985	01.07	02.01	00.28	04.18	00.90	02.01	01.14	02.96	03.07	04.20	02.77	01.76	00.31	01.20	00.12	00.34	00.00	00.00
Jul.	02.06	02.31	00.68	03.23	02.10	03.47	02.03	01.80	01.87	02.97	02.04	02.31	00.97	01.30	00.28	00.91	00.00	00.00
	02.45	01.07	01.66	03.01	01.45	04.07	03.38	03.41	02.06	03.18	01.03	01.91	01.06	01.20	00.98	01.37	00.00	00.32
Aug.	03.06	01.01	01.02	02.90	02.01	03.00	02.10	04.98	03.47	02.72	01.97	00.76	02.00	02.70	00.94	00.92	00.00	00.70
Sep.	03.65	02.45	02.63	03.07	03.84	02.80	04.86	03.78	02.84	04.61	02.72	02.90	00.63	03.71	00.70	01.17	00.40	00.90
	04.17	04.21	01.80	02.40	04.90	04.10	03.91	05.10	03.00	03.01	02.43	03.10	01.90	02.04	01.20	01.28	00.20	01.18
Oct.	03.90	01.22	03.37	03.16	03.90	02.97	03.07	04.87	02.87	03.18	01.91	02.90	01.78	02.76	01.31	02.06	00.27	01.10
	03.06	02.31	03.97	04.21	03.10	03.08	04.09	04.07	02.14	02.73	02.07	02.81	01.06	01.80	00.64	00.00	00.80	01.03
Nov.	02.76	03.10	02.84	02.10	05.60	05.67	05.67	03.07	02.06	03.98	02.11	04.10	01.70	01.30	01.07	00.78	01.07	00.48
Dec.	02.01	03.03	03.11	05.61	06.78	06.18	04.30	03.71	04.07	01.46	02.44	04.10	02.21	03.87	01.07	01.18	00.41	01.18
	01.23	02.98	02.93	06.34	07.90	07.91	05.98	05.62	02.20	02.01	01.90	03.60	01.74	03.31	00.97	01.17	00.74	00.47
Jan.	00.97	02.08	03.87	04.54	09.71	09.78	04.38	08.42	01.07	03.47	02.00	02.70	02.91	01.88	01.81	00.00	00.38	00.43
	00.42	03.61	03.47	07.56	09.87	09.88	05.07	07.39	01.08	04.31	03.11	01.90	01.81	03.33	01.07	02.31	01.80	00.18
Feb.	00.27	03.06	03.18	08.61	11.61	10.30	04.56	07.01	03.64	03.61	01.70	02.08	03.40	04.46	00.92	01.81	00.92	00.93
Mar.	01.06	02.97	03.01	07.31	08.78	13.21	04.37	06.87	01.77	04.09	01.70	02.80	02.07	01.61	02.61	02.61	01.38	00.00
	01.10	03.91	04.30	09.93	09.31	15.61	06.87	05.60	02.31	02.07	02.80	03.81	00.56	01.31	03.06	02.30	02.71	00.87
Apr.	01.32	03.81	05.08	08.21	06.38	13.91	06.07	08.73	03.74	03.71	01.07	03.90	00.96	01.31	01.08	00.71	01.10	01.40
	03.06	02.48	04.07	07.10	09.38	12.73	07.90	09.69	01.84	04.61	01.34	01.70	00.98	02.71	01.01	01.01	00.93	01.20
May	04.07	04.31	06.70	08.20	05.57	13.81	05.41	08.70	03.33	05.87	03.67	03.60	01.38	03.67	00.68	00.87	00.41	00.97
1986	03.14	03.01	05.10	06.30	04.48	13.01	03.81	07.70	02.31	04.87	03.48	04.44	00.76	02.30	00.71	00.40	00.53	00.39

S - Surface, B - Bottom

Table 11. Concentrations of dissolved organic phosphorus (µg at PO_4^{3-}-P l^{-1}) in the Cochin estuary during June 1985 to May 1986.

ion	1		2		3		4		5		6		7		8		9	
:h	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
	00.82	01.06	02.01	02.60	02.71	02.06	01.07	01.10	00.30	00.50	00.47	00.26	01.33	01.08	00.21	00.43	00.00	00.00
	01.10	01.38	00.91	03.13	02.18	03.14	01.08	01.00	00.61	00.87	00.76	00.35	01.48	01.16	00.15	00.26	00.00	00.11
	01.87	01.18	02.43	02.93	02.01	02.15	01.31	01.01	00.24	00.96	01.02	00.97	01.27	00.96	00.27	00.36	00.00	00.00
	01.41	02.56	03.00	03.41	01.97	03.80	01.46	02.07	00.77	01.02	00.68	00.87	01.48	01.06	00.50	00.21	00.00	00.00
	02.65	02.75	02.67	03.78	01.78	03.98	01.71	01.93	01.40	01.36	00.32	01.06	01.51	01.06	00.43	00.59	00.00	00.00
	03.14	03.27	02.78	02.08	03.14	04.01	02.74	02.44	02.10	00.96	01.18	00.98	01.13	01.76	00.46	00.46	00.16	00.00
	02.87	04.10	03.00	04.78	03.45	04.38	02.01	02.32	00.38	02.29	00.46	01.56	00.68	01.18	00.83	01.29	00.36	00.00
	03.41	03.61	03.68	04.08	04.41	03.08	01.70	04.18	01.16	02.66	00.96	01.06	01.87	01.36	00.75	00.81	00.20	00.00
	04.07	02.41	03.70	03.32	04.17	04.17	02.64	03.81	00.46	02.16	01.30	01.76	01.07	01.00	00.32	00.56	00.57	00.00
	02.97	02.93	03.36	04.30	02.15	05.50	00.46	03.96	00.57	03.16	01.50	02.16	01.36	01.50	00.48	01.06	00.43	00.20
	03.20	02.36	03.73	03.10	03.36	06.09	01.76	02.93	00.34	02.03	01.18	02.60	02.18	01.12	00.21	00.96	00.35	00.24
	03.90	03.18	03.20	02.93	03.41	05.86	00.76	04.87	01.30	02.30	00.96	02.01	01.31	01.33	00.57	01.28	00.26	00.09
	01.17	02.38	03.10	03.07	02.01	01.18	03.02	03.56	00.96	02.46	01.08	01.97	01.71	01.86	00.74	01.86	00.57	00.19
	02.01	01.97	03.67	03.03	01.16	04.44	01.06	03.56	00.45	02.40	00.32	01.43	01.15	01.36	00.36	00.16	00.34	00.25
	01.81	01.93	02.56	02.98	02.51	04.36	01.80	03.41	00.84	03.51	00.76	00.96	00.96	02.00	00.47	00.86	00.76	00.28
	01.71	01.97	01.76	02.06	01.71	02.87	02.00	02.97	00.87	01.95	01.18	02.76	01.44	02.06	00.97	00.47	00.18	00.68
	01.46	02.03	02.60	01.90	01.91	03.40	00.96	02.90	00.76	03.00	00.97	02.56	00.75	01.18	00.25	00.10	00.16	00.50
	02.03	02.76	01.90	01.63	00.96	02.70	01.11	02.80	01.96	02.06	01.70	02.16	00.36	00.86	00.13	00.13	00.36	00.78
	01.01	00.97	02.40	01.87	02.13	02.06	01.27	02.45	00.63	01.96	01.76	02.50	01.07	02.46	00.97	01.51	00.45	00.90
	01.87	02.06	01.60	02.16	01.46	02.03	01.14	02.06	01.31	02.16	01.56	01.88	00.86	01.38	00.97	00.63	00.75	00.70
	00.70	02.30	02.69	02.51	02.81	01.29	00.98	02.20	01.56	01.79	00.91	02.42	01.05	01.56	00.25	00.45	00.23	00.47

S - Surface, B - Bottom

ble 12. Concentrations of particulate reactive phosphorus (µg at PO_4^{3-} -P l^{-1}) in the Cochin estuary during June 1985 to May 1986.

on	1		2		3		4		5		6		7		8		9	
h	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
	00.96	01.38	01.62	01.08	01.68	01.08	00.68	01.67	00.79	01.08	01.06	00.44	00.82	00.38	00.64	00.42	00.10	00.12
	00.84	00.68	01.56	01.32	01.52	01.20	00.82	01.41	00.86	01.12	01.02	00.63	00.39	00.44	00.53	00.36	00.12	00.12
	00.81	00.96	01.20	01.68	01.30	01.55	00.76	01.22	02.81	00.96	00.82	00.46	00.36	00.55	00.49	00.12	00.12	00.33
	00.76	01.18	01.18	02.08	01.10	02.06	00.68	01.22	00.64	00.76	00.66	00.44	00.35	00.55	00.40	00.62	00.21	00.00
	00.89	00.98	01.06	01.62	00.86	01.55	00.72	00.44	00.48	00.64	00.44	00.44	00.42	00.24	00.39	00.42	00.08	00.08
	00.80	00.86	01.06	01.20	00.51	01.26	00.82	00.33	00.29	00.49	00.52	00.39	00.18	00.32	00.36	00.29	00.07	00.07
	00.74	00.88	00.86	01.22	00.68	00.99	00.76	01.08	00.38	00.69	00.66	00.32	00.26	00.18	00.38	00.28	00.00	00.00
	00.58	00.66	00.86	00.88	00.77	00.86	00.62	00.80	00.41	00.33	00.72	00.28	00.64	00.44	00.40	00.18	00.00	00.00
	00.68	00.33	00.68	00.68	00.82	00.28	00.56	01.00	00.52	00.44	00.86	00.23	00.71	00.43	00.46	00.02	00.18	00.00
	00.57	00.42	00.76	00.42	00.92	01.00	00.40	01.20	00.82	00.66	00.79	00.34	00.51	00.38	00.39	00.06	00.21	00.00
	00.39	00.66	00.39	00.36	00.40	00.33	00.68	00.66	00.63	00.58	00.43	00.44	00.68	00.16	00.39	00.01	00.07	00.00
	00.46	00.32	00.40	00.33	00.42	00.44	00.76	00.81	00.72	00.58	00.39	00.44	00.33	00.08	00.39	00.24	00.08	00.00
	00.42	00.56	00.68	00.57	00.88	00.50	00.80	00.41	00.68	00.47	00.44	00.45	00.86	00.28	00.39	00.38	00.00	00.00
	00.40	00.48	00.72	00.45	00.38	00.50	00.58	00.41	00.33	00.12	00.68	00.68	00.36	00.18	00.28	00.22	00.00	00.00
	00.59	00.32	00.56	00.76	00.40	00.82	00.46	00.00	00.30	00.47	00.82	00.63	00.33	00.76	00.16	00.16	00.00	00.00
	00.23	00.26	00.54	00.37	00.32	00.38	00.33	00.66	00.39	00.47	00.40	00.63	00.41	00.23	00.16	00.10	00.00	00.00
	00.34	00.39	00.40	00.40	00.08	00.21	00.26	00.80	00.46	00.23	00.32	00.28	00.33	00.34	00.16	00.00	00.00	00.00
	00.02	00.62	00.08	00.28	00.12	00.66	00.08	00.44	00.39	00.60	00.26	00.28	00.26	00.06	00.00	00.00	00.00	00.00
	00.44	00.34	00.26	00.18	00.00	00.40	00.02	00.44	00.24	00.72	00.11	00.44	00.12	00.08	00.00	00.08	00.00	00.00
	00.14	00.76	00.00	00.32	00.00	00.62	00.09	00.44	00.08	00.68	00.11	00.06	00.09	00.26	00.00	00.07	00.00	00.00
	00.17	00.32	00.10	00.28	00.06	00.30	00.10	00.56	00.13	00.28	00.06	00.13	00.03	00.10	00.00	00.00	00.00	00.00

S - Surface, B - Bottom

Table 13. Concentrations of total reactive phosphorus (µg at PO_4^{3-}-P l^{-1}) in the Cochin estuary during June 1985 to May 1986.

ation	1		2		3		4		5		6		7		8		9	
nth	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
n.	02.05	05.13	02.44	07.50	03.28	05.17	02.70	04.91	02.71	04.30	01.54	02.02	02.15	02.18	00.68	01.29	00.00	00.18
85	02.17	03.39	01.19	07.31	03.08	05.15	02.22	03.96	03.68	05.07	03.53	02.11	01.79	02.36	00.27	00.60	00.00	00.11
l.	03.93	03.49	03.11	06.16	04.11	05.62	03.34	02.81	02.11	03.93	03.06	03.28	02.24	02.26	00.55	01.27	00.00	00.00
	03.86	03.63	04.66	06.42	03.42	07.87	04.84	05.48	02.83	04.20	01.71	02.78	02.54	02.26	01.48	01.59	00.00	00.32
g.	05.71	03.76	03.69	06.68	03.79	06.98	03.81	06.91	04.87	04.08	02.29	01.82	03.51	03.76	01.37	01.51	00.00	00.70
p.	06.79	05.72	05.41	05.15	06.98	06.81	07.60	06.22	04.94	05.57	03.90	03.88	01.76	05.47	01.16	01.63	00.56	00.90
	07.04	08.31	04.80	07.18	08.35	08.48	05.92	07.42	03.38	05.30	02.89	04.66	02.58	03.22	02.03	02.57	00.56	01.18
t.	07.31	04.83	07.15	07.24	08.31	06.05	04.77	09.05	04.03	05.84	02.87	03.96	03.65	04.12	02.08	02.87	00.47	01.10
	07.13	04.72	07.67	07.53	07.27	07.25	06.73	07.88	02.60	04.89	03.37	04.57	02.13	02.80	00.96	00.56	01.37	01.03
v.	05.73	06.03	06.20	06.40	07.75	11.17	06.13	07.03	02.63	07.14	03.61	06.26	03.06	02.80	01.55	01.84	01.50	00.68
c.	05.21	05.39	06.84	08.71	10.14	12.27	06.06	06.64	04.41	03.49	03.62	06.70	04.39	04.99	01.28	02.14	00.76	01.42
	05.13	06.16	06.13	09.27	11.31	13.77	06.74	10.49	03.50	04.31	02.86	05.61	03.05	04.64	01.54	02.45	01.00	00.56
n.	02.14	04.46	06.97	07.61	11.72	10.96	07.40	11.98	02.03	05.93	03.08	04.67	04.62	03.74	02.55	01.86	00.95	00.62
	02.43	05.58	07.14	10.59	11.03	13.32	06.13	10.95	01.53	06.71	03.42	03.33	02.96	04.69	01.43	02.17	02.14	00.43
b.	02.08	04.99	05.74	11.59	14.12	14.66	06.36	10.42	04.48	07.12	02.46	03.04	04.36	06.46	01.39	02.67	01.68	01.21
r.	02.77	04.94	04.77	09.37	10.49	16.08	06.37	09.84	02.64	06.04	02.88	05.56	03.51	03.67	03.58	03.08	01.56	00.68
	02.56	05.94	06.90	11.83	11.22	19.01	07.83	08.50	03.07	05.07	03.77	06.37	01.31	02.49	03.31	02.40	02.87	01.37
r.	03.35	06.57	06.98	09.84	07.34	16.61	07.18	11.53	05.70	05.77	02.77	06.06	01.32	02.17	01.21	00.84	01.46	02.18
	04.07	03.45	06.47	08.97	11.51	14.79	09.17	12.14	02.47	06.57	03.10	04.20	02.05	05.17	01.98	02.52	01.38	02.10
y	05.94	06.36	08.30	10.36	07.03	15.84	06.55	10.76	04.64	08.03	05.23	05.48	02.24	05.05	01.65	01.50	01.16	01.67
6	03.84	05.31	07.79	08.81	07.29	14.30	04.79	09.90	03.87	06.66	04.39	06.86	01.81	03.86	00.96	00.86	00.76	00.86

S - Surface, B - Bottom

Table 14. Size composition and moisture (weight percentage) of sediment

Stn. No.	Season*	Nature of sediment	Sand(%) (> 63μ)	Silt(%) (4-63μ)	Clay(%) (< 4μ)	Moisture (%)	Depth° (m)
1	A	Sand	80.5	14.5	5.0	36.4	7.2
	B	Sand	85.8	8.0	6.2	32.2	
	C	Sand	80.5	12.4	7.1	30.3	
2	A	Silty clay	3.8	45.4	50.8	68.1	2.6
	B	Silty clay	7.5	37.0	55.5	63.0	
	C	Silty clay	3.5	36.3	60.2	60.2	
3	A	Clayey silt	4.1	58.3	37.6	71.0	3.4
	B	Clayey silt	3.0	53.5	43.5	66.6	
	C	Clayey silt	7.1	48.5	44.4	60.5	
4	A	Silty clay	18.0	39.5	42.5	44.6	12.2
	B	Silty clay	27.5	28.5	44.0	40.0	
	C	Silty clay	24.6	35.4	40.0	41.6	
5	A	Silty clay	20.0	34.0	46.0	51.0	5.0
	B	Silty clay	20.0	30.5	49.5	50.3	
	C	Silty clay	26.0	24.0	50.0	47.6	
6	A	Clayey sand	42.0	29.6	28.4	49.0	3.0
	B	Clayey sand	58.0	17.5	24.5	45.3	
	C	Clayey sand	48.0	20.0	32.0	41.3	
7	A	Clayey sand	63.0	19.5	17.5	44.7	3.3
	B	Clayey sand	63.0	12.9	24.1	36.3	
	C	Clayey sand	75.0	10.5	14.5	39.0	
8	A	Clayey sand	61.0	13.5	25.5	50.7	3.1
	B	Clayey sand	66.0	15.3	18.7	43.8	
	C	Clayey sand	70.0	10.0	20.0	47.0	
9	A	Clayey sand	68.3	10.7	21.0	44.8	3.2
	B	Clayey sand	62.6	9.1	28.3	42.0	
	C	Clayey sand	64.0	9.6	26.4	39.6	

* A - Monsoon, B - Postmonsoon, C - Premonsoon.

° Tidaly averaged for premonsoon.

Table. 15. Concentrations of interstitial and adsorbed sediment phosphorus (μg at PO_4^{3-}-P g^{-1}) in the Cochin estuary during June 1985 to May 1986.

tation	1		2		3		4		5		6		7		8		9	
onth	IP	AP	IP	AP	IP	AP	IP	AP	IP	AP	IP	AP	IP	AP	IP	AP	IP	AP
un.	27.65	29.31	33.33	57.10	43.71	70.11	34.66	75.10	28.81	51.14	14.38	30.13	10.10	25.31	09.99	17.34	20.10	10.10
985	21.34	21.10	36.66	51.03	51.13	75.13	30.66	60.27	30.66	55.20	20.60	35.20	13.38	21.62	16.30	19.57	20.10	13.23
ul.	23.81	27.38	35.55	43.67	40.20	71.20	36.36	61.11	26.18	51.21	19.74	34.26	15.71	28.66	19.07	20.62	17.38	15.67
	20.36	21.71	29.41	51.36	45.18	65.26	13.71	51.67	27.60	49.18	22.18	32.18	16.69	29.64	15.07	25.13	19.91	17.63
ug.	25.38	26.69	20.30	44.71	43.81	60.18	33.88	50.43	26.03	43.28	26.09	20.18	19.73	34.31	20.31	25.14	20.30	19.57
ep.	13.93	19.93	23.68	45.61	41.34	53.11	27.14	55.19	25.50	51.81	19.09	28.38	17.14	35.48	21.44	25.07	14.07	25.41
	16.27	26.44	28.71	41.37	38.46	51.17	29.13	57.37	29.04	48.31	21.44	26.61	20.40	35.83	24.60	30.26	19.07	24.58
ct.	15.46	25.63	30.80	40.46	33.56	56.18	21.10	44.42	24.09	45.44	17.42	27.37	21.61	35.89	23.71	35.32	17.48	28.60
	19.84	21.17	26.44	38.93	36.66	59.26	31.08	45.55	21.90	53.49	15.47	25.61	23.76	30.83	20.13	31.47	20.57	29.50
ov.	20.06	20.14	26.44	36.87	35.54	57.31	30.71	48.57	20.31	40.67	20.40	23.30	25.38	25.19	24.28	25.41	19.50	35.60
ec.	21.34	17.17	23.70	33.61	32.32	45.46	30.08	33.00	23.34	35.23	19.38	24.44	26.91	28.19	25.52	15.62	20.59	25.70
	14.80	16.60	23.37	34.41	27.71	42.17	19.18	35.07	20.44	30.43	17.61	20.20	20.70	21.17	20.37	16.53	21.62	15.73
n.	17.93	15.54	20.61	26.16	29.60	34.20	20.34	30.00	21.37	26.33	10.70	25.18	25.41	20.27	20.60	10.67	20.21	20.43
	11.86	13.43	24.61	30.08	32.73	38.30	24.64	37.71	20.62	19.73	11.14	19.19	21.03	19.32	20.06	19.87	21.20	19.41
eb.	10.86	10.96	21.30	27.01	31.44	35.66	25.58	31.13	19.18	17.63	13.33	18.38	25.03	19.93	19.41	17.82	19.34	20.39
ar.	13.13	12.10	20.63	25.01	29.66	28.71	25.60	29.63	20.10	20.41	14.60	27.31	20.04	19.18	18.10	20.71	14.46	21.92
	10.10	10.10	17.95	20.00	24.66	25.13	24.30	26.78	19.11	25.18	16.77	28.44	22.04	19.13	20.37	23.32	10.33	25.69
r.	09.99	07.77	14.77	15.13	25.30	26.19	20.71	25.83	22.14	20.03	13.61	13.63	25.04	15.20	20.60	19.91	13.17	24.79
	11.38	09.63	16.73	10.06	24.41	16.38	13.60	27.94	17.19	17.01	10.37	27.82	23.48	14.61	13.99	17.23	12.83	20.79
ay	10.30	11.11	20.60	19.06	20.60	21.47	17.78	30.17	19.20	14.01	19.40	20.06	20.61	10.70	17.78	14.46	11.16	19.80
86	09.81	13.70	13.38	16.06	14.72	15.43	16.81	27.44	13.38	20.31	14.47	13.40	17.17	17.40	19.63	19.83	15.70	17.18

IP - Interstitial phosphorus, AP - Adsorbed Phosphorus

Table 16. Concentrations of inorganic reactive silicate-silicon (µg at SiO_4^{4-}-Si l^{-1}) in the Cochin estuary during June 1985 to May 1986.

Station	1		2		3		4		5		6		7		8		9	
Month	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
Jun.	137.3	120.2	138.9	135.9	132.7	130.7	137.7	120.0	142.4	137.3	150.7	150.2	165.3	171.5	168.1	165.2	170.3	171.0
1985	124.9	103.3	140.3	129.0	136.6	135.7	135.6	105.1	136.4	135.2	139.6	170.0	160.8	160.5	167.4	171.1	168.8	165.3
Jul.	128.6	097.4	135.1	137.8	133.3	123.6	117.8	113.2	130.7	129.1	141.2	171.5	157.0	165.4	165.5	180.5	166.9	171.4
	111.6	090.1	120.5	117.8	131.6	128.7	121.3	090.3	127.7	120.9	140.1	165.6	154.6	161.8	163.7	182.3	167.3	180.8
Aug.	113.9	075.8	133.7	120.2	135.8	120.2	113.8	098.2	120.8	110.2	131.4	150.7	150.6	159.7	168.0	180.0	163.8	171.0
Sep.	106.8	071.7	129.6	098.2	131.3	105.5	105.4	095.1	113.9	103.7	127.1	160.8	137.7	140.7	160.0	165.2	167.5	160.8
	100.4	060.8	118.1	090.1	127.0	097.7	100.9	090.6	105.3	105.7	120.4	135.2	139.4	150.6	158.1	161.0	165.7	165.8
Oct.	091.8	050.8	100.4	093.0	117.8	083.5	103.8	077.5	107.5	099.5	114.1	117.3	137.2	140.1	157.2	150.1	165.3	153.6
	080.4	059.5	103.2	075.0	098.0	075.1	098.7	081.7	093.5	090.4	109.6	120.3	129.1	135.3	150.4	137.0	158.7	147.3
Nov.	084.4	045.9	101.8	063.6	103.2	071.1	090.8	075.4	091.5	089.3	104.5	097.1	123.1	138.4	143.6	140.5	150.4	150.6
Dec.	080.6	040.7	098.7	050.5	090.8	078.0	067.7	067.3	077.0	069.5	097.7	108.1	121.8	107.6	149.5	135.7	147.9	160.1
	070.3	045.3	089.5	059.6	083.3	060.5	075.1	041.1	071.0	075.5	090.4	105.5	120.9	120.8	135.0	118.9	141.3	137.5
Jan.	062.7	051.7	091.4	051.3	080.6	063.3	071.8	049.9	061.4	071.1	087.5	093.6	117.6	117.7	130.0	105.3	133.4	131.3
	057.3	060.8	075.3	047.2	073.8	049.3	069.5	056.4	065.5	060.1	088.7	090.0	105.5	106.6	128.0	128.3	135.1	135.5
Feb.	053.7	053.3	080.9	045.7	088.9	045.2	076.4	060.3	067.6	061.8	080.3	066.7	097.3	110.7	110.3	114.6	133.6	120.3
Mar.	043.8	045.5	071.1	042.9	060.5	049.2	071.6	063.3	064.0	057.8	060.1	077.8	090.6	118.6	123.4	117.7	130.2	127.4
	048.7	030.5	060.7	040.9	040.3	047.1	068.7	060.6	060.8	045.6	077.0	080.0	093.3	105.4	109.6	100.0	123.7	119.5
Apr.	030.8	038.7	058.3	030.7	051.7	030.0	063.0	050.4	040.6	043.3	075.3	076.0	090.7	097.7	098.7	105.3	128.2	120.5
	034.4	043.6	045.6	038.2	045.3	038.8	038.2	047.5	053.5	030.2	063.9	071.8	083.7	093.1	109.9	097.5	115.3	118.6
May	031.0	038.0	030.5	045.1	030.6	045.6	030.8	043.6	045.3	041.2	070.9	070.9	090.3	090.3	101.7	107.6	122.1	105.7
986	037.6	039.1	040.9	043.4	028.2	040.1	028.8	030.5	046.8	043.4	071.2	065.4	083.1	089.9	102.7	109.1	113.9	117.8

S - Surface, B - Bottom